South Dakota State University

Open PRAIRIE: Open Public Research Access Institutional Repository and Information Exchange

Electronic Theses and Dissertations

1975

Interactions of Rhenium(V) Chloride and Oxotrichlorobis(Triphenlyphosphine)Rhenium(V) With Selected Solvents

Paul Luther Holm

Follow this and additional works at: https://openprairie.sdstate.edu/etd

 Part of the Chemistry Commons

Recommended Citation

Holm, Paul Luther, "Interactions of Rhenium(V) Chloride and Oxotrichlorobis(Triphenlyphosphine)Rhenium(V) With Selected Solvents" (1975). *Electronic Theses and Dissertations*. 5539.
https://openprairie.sdstate.edu/etd/5539

This Dissertation - Open Access is brought to you for free and open access by Open PRAIRIE: Open Public Research Access Institutional Repository and Information Exchange. It has been accepted for inclusion in Electronic Theses and Dissertations by an authorized administrator of Open PRAIRIE: Open Public Research Access Institutional Repository and Information Exchange. For more information, please contact michael.biondo@sdstate.edu.

INTERACTIONS OF RHENIUM(V) CHLORIDE AND OXOTRICHLOROBIS(TRIPHENYLPHOSPHINE)RHENIUM(V) WITH SELECTED SOLVENTS

BY

PAUL LUTHER HOLM

A thesis submitted
in partial fulfillment of the requirements for the
degree Doctor of Philosophy, Major in
Chemistry, South Dakota
State University

1975

SOUTH DAKOTA STATE UNIVERSITY LIBRARY

168

INTERACTIONS OF RHENIUM(V) CHLORIDE AND OXOTRICHLOROBIS(TRIPHENYLPHOSPHINE)RHENIUM(V) WITH SELECTED SOLVENTS

This thesis is approved as a creditable and independent investigation by a candidate for the degree, Doctor of Philosophy, and is acceptable for meeting the thesis requirements for this degree, but without implying that the conclusions reached by the candidate are necessarily the conclusions of the major department.

_____ _____

Thesis Advisor Date

_____ _____

Head, Chemistry Department Date

INTERACTIONS OF RHENIUM(V) CHLORIDE AND OXOTRICHLOROBIS(TRIPHENYLPHOSPHINE)RHENIUM(V) WITH SELECTED SOLVENTS

Abstract

PAUL LUTHER HOLM

Under the supervision of Dr. Henry Gehrke, Jr.

The purpose of this study was to examine the solution interactions of rhenium(V) chloride and oxotrichlorobis(triphenylphosphine)rhenium(V) in a continuation of studies of rhenium(V) chemistry. These goals were accomplished using vacuum line and Schlenk tube techniques.

As a result of this work, rhenium(V) chloride was found to dissolve with reaction in 1,4-dioxane, diethyl ether and acetone. There was only a very small amount of rhenium(V) chloride which dissolved in carbon tetrachloride, chloroform and cyclohexane. Part of what did dissolve was shown by electronic and infrared spectroscopy to be oxotetrachlororhenium(VI) which was present as an impurity in small amounts. Oxotetrachlororhenium(VI) reacts with triphenylphosphine in carbon tetrachloride to form tetrachloro(triphenylphosphinetriphenylphosphine oxide) rhenium(IV). The infrared spectra of rhenium(V) chloride was found to differ from reports in the literature. Supported by good correlations between x-ray powder data and calculated d- spacings from the crystal structure, the infrared spectrum in this study was more representative of rhenium(V) chloride than those reported. An examination of "aged" rhenium(V) chloride was made, which indicated that the differences in

reactions of "aged" rhenium(V) chloride, and fresh rhenium(V) chloride are due to partial hydrolysis of rhenium(V) chloride.

The reaction of rhenium(V) chloride, in acetone, with pyridine was examined. It was found that a stoichiometric amount of pyridine was required to obtain μ-oxodioxotetrachlorotetrakis(pyridine) dirhenium(V) from either "aged" rhenium(V) chloride or fresh rhenium(V) chloride. An excess of pyridine caused the formation of dioxotetrakis(pyridine)-rhenium(V) chloride dihydrate with either "aged" or fresh rhenium(V) chloride.

Sealed tube reactions of oxotrichlorobis(triphenylphosphine)-rhenium(V) with chloroform produced a variety of products which depended on the purity of the chloroform and the presence of excess triphenylphosphine. Tetrachlorobis(triphenylphosphine oxide)rhenium(IV) and tetrachlorobis(triphenylphosphine) were produced when stock chloroform was used. When stock chloroform and excess triphenylphosphine were used, bis(methyltriphenylphosphonium) hexachlororhenate was formed. Pure chloroform, excess triphenylphosphine and oxotrichlorobis(triphenylphosphine)rhenium(V) reacted, producing three products. Tentative formulations were suggested but required further work before a more positive formulation could be made.

A proposed sequence of reactions based on the reaction of bromoform with triphenylphosphine was examined and was found to correlate much of the observed data from sealed tube reactions of oxotrichlorobis-(triphenylphosphine)rhenium(V) with chloroform.

ACKNOWLEDGEMENTS

For the help and encouragement received from undergraduate students, graduate students, faculty, and support personnel in the Department of Chemistry at South Dakota State University. A special acknowledgement to Mr. Floyd Melrose for his help with the maintenance of instruments, to Mr. Ranson Ashmore who was always ready to fabricate and repair glass apparatus, and to Dr. David Hilderbrand for his help with the manuscript.

For the guidance received from Dr. Henry Gehrke, Jr. in his direction of this research.

For the superb work of Ms. Helen Rosheim in typing and duplicating the manuscript.

Especially, I wish to acknowledge the constant support of my wife, Alice, who in the face of discouragement was able to encourage, who was a prop, a prod and a sounding board.

And my daughters, Katherine and Karin, who made more sacrifices for this work than they realize.

The National Science Foundation who supported part of this work under grant no. GP 11027.

TABLE OF CONTENTS

	Page
INTRODUCTION	1
HISTORICAL	3
Rhenium(V) Chloride	4
Structure	5
Reactions	7
Reactions with Organic Ligands	8
Other Transition Metal Pentachlorides	10
Preparation	10
Structures	10
Relationships Between Metal Pentachlorides	11
Reactions of Metal Pentachlorides	12
Reactions of Rhenium(V) Chloride with Triphenylphosphine	14
Sealed Tube Reactions of Oxotrichlorobis(triphenylphosphine)rhenium(V)	16
Reactions with Chloroform	16
EXPERIMENTAL	18
Infrared Spectra	18
Mass Spectra	19
Electronic Spectra	20
Molecular Mass	20
Nuclear Magnetic Resonance Spectra	20
X-ray Photographs	20
Rhenium Analyses	21
Chlorine Analyses	21
Other Analyses	21

Page

Rhenium Metal..... 22

Ammonium Perrhenate..... 22

Triphenylphosphine..... 22

Oxotrichlorobis(triphenylphosphine)rhenium(V)..... 22

Solvent Purification..... 22

Carbon Tetrachloride..... 24
Chloroform..... 25
Cyclohexane..... 25
Acetone..... 26
1,4-dioxane..... 26
Diethyl Ether..... 26
2-butanone..... 26

Aluminum Oxide..... 26

Rhenium(V) Chloride..... 27

Oxotetrachlororhenium(VI)..... 29

Vacuum System..... 29

Solution Experiments..... 31

Schlenk Tubes..... 34

Schlenk Tube Experiments..... 37

Glove Box..... 37

Studies into the Nature of "Aged" Rhenium(V) Chloride..... 39

Vacuum Line Experiments with Rhenium(V) Chloride..... 39

Carbon Tetrachloride..... 39
Chloroform..... 44
Cyclohexane..... 46
1,4-dioxane..... 47
Diethyl Ether..... 48
Acetone..... 49
Oxotetrachlororhenium(VI) and Carbon Tetrachloride.... 50

Page

Schlenk Tube Experiments with Rhenium(V) Chloride and Carbon Tetrachloride..... 51

Schlenk Tube Experiments with Oxotetrachlororhenium(VI) and Carbon Tetrachloride..... 52

Reaction of Rhenium(V) Chloride in Acetone with Excess Pyridine..... 53

Reaction of Rhenium(V) Chloride in Acetone with the Stoichiometric Amount of Pyridine..... 54

Reaction of "Aged" Rhenium(V) Chloride in Acetone with the Stoichiometric Amount of Pyridine..... 55

Reaction of Rhenium(V) Chloride with Acetic Acid..... 56

Sealed Tube Reactions..... 57

Sealed Tube Reactions of Oxotrichlorobis(triphenylphosphine)rhenium(V) with Chloroform..... 58

Reaction I..... 59
Reaction II..... 60
Reaction III..... 61
Reaction IV..... 62
Reaction V..... 63
Reaction VI..... 67

Sealed Tube Reaction of Oxotrichlorobis(triphenylphosphine)rhenium(V) with Acetone..... 68

Sealed Tube Reaction of Oxotrichlorobis(triphenylphosphine)rhenium(V) with 2-butanone..... 68

DISCUSSION..... 71

Rhenium(V) Chloride..... 71

Melting Point..... 71
Infrared Spectra..... 72
X-ray Analysis..... 77

"Aged" Rhenium(V) Chloride..... 78

X-ray Analysis 81
Infrared Spectra..... 83
Elemental Analysis..... 84

Page

Solvent Studies with Rhenium(V) Chloride..... 87

Carbon Tetrachloride..... 89
Reaction of Triphenylphosphine with Oxotetrachloro-rhenium(VI)..... 94
Chloroform..... 101
Cyclohexane..... 102
Summary of Solvent Studies..... 104

Adduct Formation Studies..... 105

1,4-dioxane..... 106
Diethyl Ether..... 107
Acetone..... 109
Summary of Adduct Preparation Experiments..... 111

Evaluation of the Apparatus Used..... 112

Acetic Acid and Rhenium(V) Chloride..... 115

Rhenium(V) Chloride in Acetone with Pyridine..... 117

Sealed Tube Reactions..... 121

Sealed Tube Reactions of Chloroform and Oxotrichloro-bis(triphenylphosphine)rhenium(V)..... 121

Stock Chloroform..... 121
Stock Chloroform with Excess Triphenylphosphine.. 124
Pure Chloroform with Excess Triphenylphosphine... 128

1. Dichloromethyltriphenylphosphonium pentachloro(triphenylphosphine oxide)-rhenate(IV)..... 129
2. White Powder..... 135

a) Unrecrystallized Material..... 135
b) Recrystallized Material..... 137
c) Recrystallized Material Heated at Reduced Pressure..... 137
d) Recrystallized Material Heated at One Atmosphere..... 138
e) Derivatives of the Recrystallized Material..... 139
f) Formulation of the Recrystallized White Powder..... 139

Page

(1) Trichloromethyltriphenylphosphonium chloride..... 139
(2) Chloroform Adduct..... 140
(3) Dihydroxymethyltriphenylphosphonium chloride..... 140
(4) Methylenebis(triphenylphosphonium chloride)..... 141

3. Purple Product of Reaction of Oxotrichlorobis(triphenylphosphine)rhenium(V) with Chloroform..... 144

Sealed Tube Reaction of Oxotrichlorobis(triphenylphosphine)rhenium(V) with Acetone..... 145

Sealed Tube Reaction of Oxotrichlorobis(triphenylphosphine)rhenium(V) with 2-butanone..... 145

SUMMARY..... 149

APPENDIX..... 154

Tables..... 155
Figures..... 159

LIST OF REFERENCES CITED..... 173

LIST OF TABLES

Table		Page
I.	Physical Properties of Rhenium	4
II.	Preparations of Rhenium(V) Chloride	5
III.	Inorganic Reactions of Rhenium(V) Chloride	7
IV.	Reactions in Which Oxygen is Abstracted	9
V.	Reactions in Which Ligand Substitution Occurs	9
VI.	Preparation of Metal Pentachlorides	11
VII.	Reactions of Metal Pentachlorides	13
VIII.	Products Formed in the Reaction of Rhenium(V) Chloride in Acetone with Triphenylphosphine	15
IX.	X-ray Powder Data of the "Aging" Process of Rhenium(V) Chloride	40
X.	Infrared Spectrum of "Aged" Rhenium(V) Chloride	41
XI.	Analysis Results of the "Aging" Process of Rhenium(V) Chloride	42
XII.	Results of Carbon Tetrachloride Solution Experiment	43
XIII.	Results of Chloroform Solution Experiment	45
XIV.	Results of Cyclohexane Solution Experiment	47
XV.	Results of 1,4-dioxane Solution Experiment	48
XVI.	Results of Diethyl Ether Solution Experiment	49
XVII.	Results of Acetone Solution Experiment	50
XVIII.	Results of Oxotetrachlororhenium(VI) and Carbon Tetrachloride Experiment	51
XIX.	Chloroform Used in Sealed Tube Reactions	58

Table		Page
XX.	Summary of Experimental Results on White Product of Reaction of Oxotrichlorobis(triphenylphosphine)-rhenium(V) and Triphenylphosphine in Purified Chloroform	66
XXI.	Infrared Spectrum of Rhenium(V) Chloride	74
XXII.	Comparison of Calculated and Observed d- Spacings of Rhenium(V) Chloride	79
XXIII.	Rhenium Content for Suggested Species Present in "Aged" Rhenium(V) Chloride	86
XXIV.	Rhenium-Chlorine Infrared Absorption Frequency and Color of Some Complexes of the General Form $ReCl_4L_2$	96
XXV.	Comparison of Amount of $ReOCl_4$ Required to Form $ReCl_4[(C_6H_5)_3P][(C_6H_5)_3PO]$	98
XXVI.	Reactions of Triphenylphosphine with Chlorinated Hydrocarbons	126
XXVII.	Proposed Reaction Sequence	127
XXVIII.	d- Values for Oxotetrachlororhenium(VI)	155
XXIX.	d- Values for Rhenium(III) Chloride	156
XXX.	d- Values for Rhenium(IV) Chloride	157
XXXI.	d- Values for Solute Recovered from Carbon Tetrachloride Solution	158

LIST OF FIGURES

Figure		Page
1.	Structure of Rhenium(V) Chloride	6
2.	Solvent Purification Apparatus	23
3.	Vials for Storing Rhenium(V) Chloride	28
4.	Nitrogen Purification System	30
5.	Vacuum-line Filtration Apparatus	33
6.	Examples of Schlenk Tube Apparatus	35
7.	Buffer Gas Apparatus	36
8.	Path of Gas Flow in Schlenk Tube Apparatus	38
9.	Tube Used for Sealed Tube Experiments	57
10.	Ammonium Perrhenate	159
11.	Triphenylphosphine	159
12.	Triphenylphosphine Oxide	159
13.	Oxotrichlorobis(triphenylphosphine)rhenium(V)	160
14.	Rhenium(V) Chloride	160
15.	Rhenium(V) Chloride 2X Abscissa Expansion of the 500 cm^{-1} to 250 cm^{-1} Region	160
16.	Oxotetrachlororhenium(VI)	161
17.	Oxotetrachlororhenium(VI) 2X Abscissa Expansion of the 500 cm^{-1} to 250 cm^{-1} Region	161
18.	"Aged" Rhenium(V) Chloride	161
19.	Rhenium Dioxide	162
20.	Rhenium(III) Chloride	162
21.	Rhenium(III) Chloride 2X Abscissa Expansion of the 500 cm^{-1} to 250 cm^{-1} Region	162

Figure Page

43. Tetraphenylborate Salt of White Powder..... 170

44. Sodium Tetraphenylborate..... 170

45. Perrhenate Salt of White Powder..... 170

46. Purple Powder Produced in Chloroform Reaction..... 171

47. Dichloromethyltriphenylphosphine Pentachloro(triphenylphosphine oxide)rhenium(IV)..... 171

48. Trichloro(triphenylphosphine oxide)rhenium(III)..... 171

49. Green Solid Produced from 2-butanone Reaction..... 172

INTRODUCTION

The importance of the role of the solvent in chemical reactions has long been recognized. At South Dakota State University, the importance of the solvent and its purity has been observed in reactions involving rhenium(V) chloride and oxotrichlorobis(triphenylphosphine)-rhenium(V). In addition, it has been noted that fresh rhenium(V) chloride reactions are different than those of "aged" rhenium(V) chloride in the same solvent. Thus the solvent purity, the solubility of rhenium(V) chloride in the solvent, the previous use of the solvent with metal pentachlorides, and the possible reaction of the solvent to form an adduct with rhenium(V) chloride were factors in choosing the solvents; carbon tetrachloride, chloroform, cyclohexane, 1,4-dioxane, and diethyl ether for use in this study.

Apparatus used in the study needed to maintain an anhydrous condition because of the hydrolytic instability of rhenium(V) chloride. Although water can be excluded in a high vacuum system, the solvent volumn used is limited. Somewhat larger volumes of solvent can be used in "Schlenk tube" apparatus but this apparatus is somewhat less effective in maintaining an anhydrous condition than is the vacuum system. The glove box is essential in preparing samples for analysis even though less effective in maintaining an anhydrous condition than either of the previously mentioned apparatus.

Intermediate species which may be formed during a reaction with a solvent may be unstable. Such intermediates are of interest and can

sometimes be trapped by the use of a stabilizing ligand. Triphenylphosphine is such a ligand and the body of literature on triphenylphosphine complexes would aid the identification of products which would be isolated.

The study is divided into four parts: 1. The analysis of pure rhenium(V) chloride, 2. The nature of "aged" rhenium(V) chloride, 3. The interaction of the solvents with rhenium(V) chloride, and 4. The reactions, in sealed tubes, of oxotrichlorobis(triphenylphosphine)-rhenium(V) with solvents.

HISTORICAL

Rhenium was discovered by Noddack et al. (1) in 1925. Between that time and 1960, little research was conducted into the chemistry of rhenium because of its scarcity. Since 1960 there has been considerable research activity in the chemistry of rhenium. An indication of this activity can be found in recent reviews (2)(3) and monographs (4)(5). As the chemistry of rhenium has been studied several cluster compounds have been observed. It has been found that both rhenium(III) chloride (6) and rhenium(IV) chloride (7) exist as cluster compounds. These observations led to the prediction that rhenium(V) chloride might be a cluster compound. The limited amount of research in rhenium(V) chloride can be traced to the difficulties encountered in handling this hydrolytically unstable compound.

To gain insight into the structure of rhenium(V) chloride by studying its behavior in solution, it is necessary to find a solvent with which rhenium(V) chloride does not interact. That the choice of solvent is not a trivial exercise has been shown by Gehrke and Eastland (8) in studies on solutions of rhenium(V) chloride in acetone and benzene.

The importance of solvent choice can be illustrated by a study of Colton and Tompkins (9). In this study it was suggested that tungsten(V) chloride had a trimeric structure, $[W_3Cl_{12}]Cl_3$, similar to rhenium(III) chloride. This conclusion was based on the

observation that a solution of tungsten(V) chloride in acetonitrile indicated the existence of three ionic chloride ions. In addition, the magnetic properties of tungsten(V) chloride in acetonitrile were interpreted on the basis of a trinuclear cluster formulation. Later, tungsten(V) chloride was shown (10) to react with acetonitrile according to the reaction

$$WCl_5 + 2CH_3CN \longrightarrow [WCl_4(CH_3CN)_2]Cl.$$

This suggested that the species which Colton and Tompkins (9) were, in fact, examining was the solution containing $[WCl_4(CH_3CN)_2]^{1+}$ and Cl^{1-} ions. For this reason, it is important that a nonreacting solvent for rhenium(V) chloride be found.

RHENIUM(V) CHLORIDE

Some of the physical properties of rhenium(V) chloride are shown in Table I. Table II summarizes some of the methods of

TABLE I

PHYSICAL PROPERTIES OF RHENIUM(V) CHLORIDE

melting point	260°C (2)
boiling point	decomposes to Re_3Cl_9 (5)
density	3.98 gm./cm.^{3} (11)
magnetic moment	2.21 B.M. (5)

preparation of rhenium(V) chloride. The most common method of preparation is reaction a, Table II.

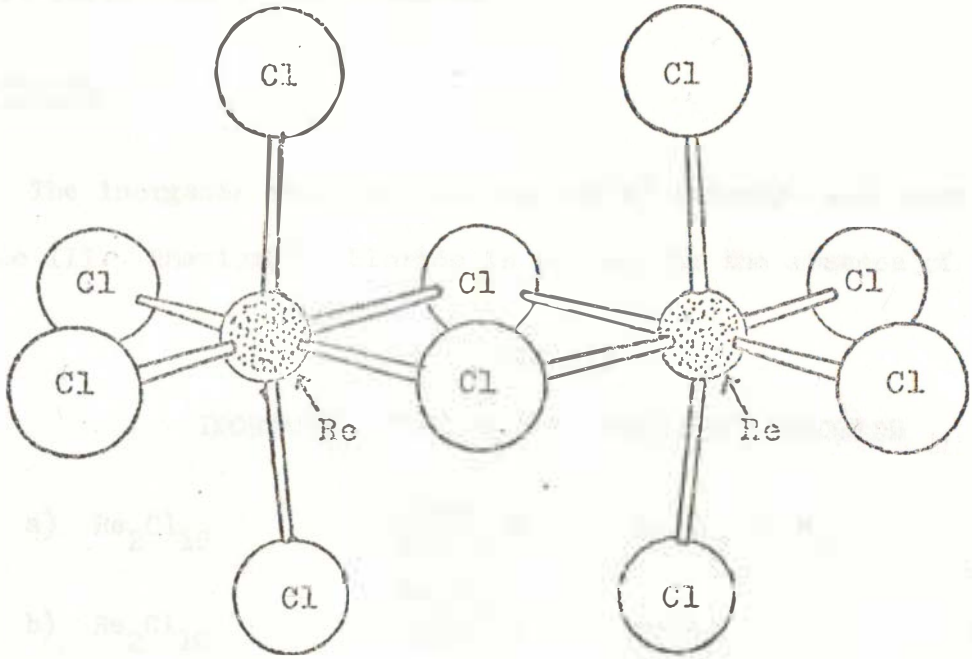


Figure 1

Structure of Rhenium(V) Chloride

Additional evidence which supports the dimeric structure has been obtained by Smardzewski (20) and Edwards and Ward (21). They have interpreted the observed infrared spectra on the basis of D_{2h} symmetry. A comparison of the calculated and observed absorption frequencies by Smardzewski shows good correlation. In both studies alternative structures, the monomeric trigonal bipyramid (with D_{3h} symmetry) and the tetragonal pyramid (with C_{4v} symmetry), could

be ruled out. D_{3h} symmetry would predict a maximum of five infrared active bands and C_{4v} symmetry would predict six infrared active bands while twelve bands were observed.

REACTIONS

The inorganic reactions of rhenium(V) chloride are shown in Table III. Rhenium(V) chloride is stable, in the absence of moisture,

TABLE III

INORGANIC REACTIONS OF RHENIUM(V) CHLORIDE

a)	$Re_2Cl_{10} \xrightarrow[\text{dry } N_2]{\text{heat}}$	$Re_3Cl_9 + Cl_2$	(22)
b)	$Re_2Cl_{10} \xrightarrow[\text{heat}]{Re_3Cl_9}$	$ReCl_4$	(23)
c)	$Re_2Cl_{10} + O_2 \xrightarrow[\text{dry}]{\text{heat}}$	$ReOCl_4 + ReO_3Cl$	(24)
d)	$Re_2Cl_{10} + NaOH_{(aq)} \longrightarrow$	$ReO_2 \cdot 2H_2O + NaReO_4$	(25)
e)	$Re_2Cl_{10} + H_2O \longrightarrow$	Re(IV) + Re(VII)	(5)
f)	$Re_2Cl_{10} + HCl_{(aq)} \longrightarrow$	$ReOCl_5^{1-}$	(5)

at temperatures below about 260° C. However, above 300°C, in a dry nitrogen atmosphere, rhenium(III) chloride is formed. Reactions a, b and c, in Table III, are important because they represent ways in which impurities may be introduced into rhenium(V) chloride. The importance of reactions d and, particularly, e and f, in Table III, lies in the possibility that solvents may contain water.

REACTIONS WITH ORGANIC LIQUIDS

Rhenium(V) chloride reacts with many organic liquids. The results of such reactions can be generally described by one of the following interactions: 1) substance may dissolve without reaction; 2) simple adducts, $ReCl_5L$ (L = a monodentate ligand), may be formed; 3) replacement reactions might occur in which oxygen is abstracted from the solvent or water together with ligand replacement in the coordination sphere; 4) replacement reactions without oxygen abstraction may take place. In so far as possible, examples of each of these modes of reaction will be considered.

Horner et al. (26) have been able to recover rhenium(V) chloride from high temperature reactions of perrhenates with carbon tetrachloride. The resulting hexachlororhenate was contaminated with rhenium(V) chloride, which could be extracted by and recovered from carbon tetrachloride.

In the infrared studies of Smardzewski (20), spectra of rhenium(V) chloride obtained in cyclohexane solution compared well with spectra obtained from mulled samples. Therefore, it was concluded that the species in solution was rhenium(V) chloride.

There are no examples of simple adduct formation between rhenium(V) chloride and potential ligands. There are, however, examples of reactions in which oxygen is abstracted replacing one of the chloride ions and a ligand is added to the coordination sphere. These examples are shown in Table IV. In both cases it was water

TABLE IV

REACTIONS IN WHICH OXYGEN IS ABSTRACTED

a) $Re_2Cl_{10} + C_5H_5N + H_2O \xrightarrow{\text{acetone}} [ReO_2(C_5H_5N)_4]Cl \cdot 2H_2O + Re_2O_3Cl_4(C_5H_5N)_4$ (27)

b) $Re_2C_{10} + (C_6H_5)_3P + H_2O \xrightarrow{\text{acetone}} ReOCl_3[(C_6H_5)_3P]_2$ (28)

which donated the oxygen. Cotton et al. (29) were able to duplicate reaction a if they used rhenium(V) chloride which had been "aged" for one week.

Examples of reactions where ligand substitution occurs with no oxygen abstraction are shown in Table V. Because the reaction

TABLE V

REACTIONS IN WHICH LIGAND SUBSTITUTION OCCURS

Ligand	Product	Reference
RCN R=methyl, propyl, phenyl	$ReCl_4(RCN)_2$	(30)
Cyclic ethers thioxane, dioxane, tetrahydrofuran	$ReCl_4(L)_2$	(31)

between 1,4-dioxane and molybdenum(V) chloride (32) led to oxygen abstraction, it was surprising that oxygen abstraction did not occur with rhenium(V) chloride (31).

The preceding has pointed out ways in which rhenium(V) chloride reacts. It indicates that the chemistry of rhenium(V) chloride is determined by the labile nature of chlorine in its coordination sphere. It was also noted that water in solvents is very important to the way in which reactions proceed.

OTHER TRANSITION METAL PENTACHLORIDES

There are similarities between rhenium(V) chloride and other metal pentachlorides. Therefore a comparison of solvent interactions of the various pentachlorides might shed some light on ways in which rhenium(V) chloride could be expected to behave.

PREPARATION

The preparation of various metal pentachlorides is outlined in Table VI.

STRUCTURES

It has already been pointed out that the structure of niobium, molybdenum and rhenium pentachlorides are similar. Tantalum(V) chloride has been shown to have a similar structure (39). The fact that the structures of the pentachlorides are similar does not require that other properties be similar, but it does provide a reason for considering chemical similarity.

TABLE VI

PREPARATION OF METAL PENTACHLORIDES

Reaction	Metals	Reference
$M + Cl_2 \longrightarrow MCl_5$	Rhenium	(12)(13)
	Molybdenum	(33)
	Niobium	(34)
	Tantalum	(34)
Metal oxide + $SOCl_2 \longrightarrow MCl_5$	Molybdenum	(35)
	Niobium	(36)
	Tantalum	(36)
Metal oxide + $CCl_4 \longrightarrow MCl_5$	Rhenium	(14)
	Molybdenum	(37)
	Niobium	(38)
	Tantalum	(38)

RELATIONSHIPS BETWEEN METAL PENTACHLORIDES

It is difficult to draw any general and reliable relationship between rhenium(V) chloride and other transition metal pentachlorides. The periodic law predicts that rhenium(V) chloride and technetium(V) chloride should be closely related. However, technetium(V) chloride has never been prepared. Horizontal relationships seldom occur and this is certainly true with the metal pentachlorides. Relationships which do exist must be considered exceptions. Rouschias (2) states that there are distant similarities between isoelectronic complexes of rhenium and molybdenum. This statement may be expanded to include similarities between rhenium(V) chloride and molybdenum(V) chloride. It is for these reasons that rhenium, in general, and

rhenium(V) chloride, in particular, have been studied by themselves. It is also for these reasons that it is not surprising when reactions of rhenium(V) chloride and other metal pentachlorides are found to be different.

REACTIONS OF METAL PENTACHLORIDES

To look at the possibility of chemical similarity of metal pentachlorides, a summary of reactions is tabulated in Table VII. This summary of reactions can be put into perspective by considering the same four interactions as were outlined in reference to rhenium reactions: 1) The chloride may form a simple adduct, for example when 1,4-dioxane reacts with molybdenum, niobium and tantalum pentachlorides. 2) A replacement reaction may occur in which chlorine is removed and replaced by the reactant, as is the case with acetic acid and molybdenum. 3) Replacement reactions in which the oxidation number of the metal is reduced, as for niobium and tantalum reacting with pyridine as well as the ether reaction and also the nitrile reaction with molybdenum.

From this summary presentation of reactions, similarities are indeed noted between rhenium(V) chloride and other metal pentachlorides. Molybdenum and rhenium pentachloride form the same nitrile complex. To be sure, differences do exist, yet the fact that there are similarities at all makes it possible to consider research which has been done with other metal pentachlorides.

TABLE VII

REACTIONS OF METAL PENTACHLORIDES

Reactant	Metal	Product	References
H_2O	Mo	$MoOCl_3$	(40)
	Nb	$HNbO_4$	(41)
	Ta	$HTaO_4$	(41)
H_2O + HCl	Mo	No Reaction	
	Nb	$NbOCl_3$	(41)
	Ta	$TaOCl_3$	(41)
Pyridine	Mo	$MoCl_5 \cdot XC_5H_5N$ X = 3, 4 or 5	(33)
	Nb	$NbCl_4(C_5H_5N)_2$	(42)
	Ta	$TaCl_4(C_5H_5N)_2$	(42)
Acetic Acid	Mo	$MoCl_3(OOCCH_3)_2$	(43)
1,4-dioxane	Mo	$MoCl_5(dioxane)_2$	(32)
	Nb	$NbCl_5(dioxane)$	(44)
	Ta	$TaCl_5(dioxane)$	(44)
RCN	Mo	$MoCl_4(RCN)_2$	(10)
	Nb	$NbCl_5(RCN)$	(44)
Diethyl ether	Nb	$NbCl_4(ether)_2$	(45)
	Ta	$TaCl_4(ether)_2$	(45)

305281 SOUTH DAKOTA STATE UNIVERSITY LIBRARY

Very important relationships to look at are those in which no reaction occurs between the solvent and the metal pentachloride. Kepert and Mandyczewski (32) found that molybdenum(V) chloride could be recovered, unchanged, from carbon tetrachloride. However, after extended lengths of time, chlorine-deficient products which approximated molybdenum(IV) chloride were recovered. Fairbrother et al. (46) found that niobium(V) chloride would dissolve in benzene, without reaction to produce a red solution. The same study showed that tantalum(V) chloride dissolves in benzene, cyclohexane, toluene, m-xylene, mesitylene and carbon tetrachloride. There seems to be some similarity between rhenium, molybdenum and tantalum pentachlorides. Each are reported to dissolve, without reaction, in cyclohexane. Rhenium and tantalum pentachloride are also reported to dissolve in carbon tetrachloride.

REACTIONS OF RHENIUM(V) CHLORIDE WITH TRIPHENYLPHOSPHINE

Since there is often the possibility of producing unstable intermediates in the course of solution studies, it would be useful to be able to trap the intermediate so that it might be isolated and elucidated. One possible way to accomplish this is to use a ligand which might stabilize the intermediate. One such ligand is triphenylphosphine. Triphenylphosphine is attractive not only because of its stabilizing influence, but also because of the large body of literature which describes various rhenium triphenylphosphine complexes. Such reactions have been reviewed by Rouschias (2).

Studies which have been carried out show the importance of the solvent and its purity. Johnson et al. (28) studied the reaction between rhenium(V) chloride and triphenylphosphine using dry acetone or methylene chloride as the solvent.

Gehrke and Eastland (8) investigated the acetone reactions in more detail. Acetone solutions of rhenium(V) chloride and triphenylphosphine resulted in a mixture of products. Their results are shown in Table VIII. The amounts of the various products were found

TABLE VIII

PRODUCTS FORMED IN REACTION

$$Re_2Cl_{10} + (C_6H_5)_3P \xrightarrow[\text{Acetone}]{}$$

Product	Color	Yield in dry Acetone	Yield in wet Acetone
$ReCl_4[(C_6H_5)_3P]_2$	Red	25%	.6%
$ReOCl_3[(C_6H_5)P]_2$	Green	Trace	28%
$\left[CH_3\overset{O}{\overset{\|}{C}}CH_2\overset{CH_3}{\overset{\|}{C}}P(C_6H_5)_3\right]\left[ReCl_5(C_6H_5)_3P\right]$	Yellow	12.6%	13%
$\left[CH_3\overset{O}{\overset{\|}{C}}CH_2\overset{CH_3}{\overset{\|}{C}}P(C_6H_5)_3\right]_2 Re_2Cl_8$ and $\left[CH_3\overset{O}{\overset{\|}{C}}CH_2\overset{CH_3}{\overset{\|}{C}}P(C_6H_5)_3\right]_2 Re_2Cl_9$	Purple	2%	.3%

to be dependent on the presence or absence of water, as shown in the table. The number of products produced can account for the erroneous formulation of Johnson et al. (28).

Gehrke and Eastland continued their (8) study of solvents and solvent interactions with rhenium(V) chloride and triphenylphosphine using benzene as a solvent. They found that bis(triphenylphosphonium) nonachlorodirhenate(III-IV), $\left[(C_6H_5)_3PH\right]_2Re_2Cl_9$, was produced. This reaction was attributed to the reaction of a small amount of water with rhenium(V) chloride. When wet benzene was used the major product was shown to be oxotrichlorobis(triphenylphosphine)rhenium(V), $ReOCl_3\left[(C_6H_5)_3P\right]_2$.

SEALED TUBE REACTIONS OF OXOTRICHLOROBIS(TRIPHENYLPHOSPHINE)RHENIUM(V)

Reactions in sealed tubes are of interest because the higher temperatures and pressures which are produced can lead to novel compounds. There has been some research which involved the use of sealed tubes (47). This work points out the importance of the solvent and its purity.

REACTIONS WITH CHLOROFORM

In work done by Leitheiser (47), it was found that when oxotrichlorobis(triphenylphosphine)rhenium(V), $ReOCl_3\left[(C_6H_5)_3P\right]_2$, was heated with chloroform at elevated temperatures, a mixture of tetrachlorobis-(triphenylphosphine)rhenium(IV), $ReCl_4\left[(C_6H_5)_3P\right]_2$, and tetrachlorobis-(triphenylphosphineoxide)rhenium(IV), $ReCl_4\left[(C_6H_5)_3PO\right]_2$, was produced.

When stock chloroform was used the amount of tetrachlorobis(triphenylphosphine)rhenium(IV), $ReCl_4[(C_6H_5)_3P]_2$, was a minor product while the phosphine oxide was produced in at least a four-fold greater amount than the phosphine. The relative amount of each product was dependent on the time the reaction mixture was heated. Longer reaction times resulted in almost quantitative conversion of the oxotrichlorobis(triphenylphosphine)rhenium(V), $ReOCl_3[(C_6H_5)_3P]_2$, to tetrachlorobis(triphenylphosphineoxide)rhenium(IV), $ReCl_4[(C_6H_5)_3PO]_2$. However, if chloroform was purified to remove water and ethanol the amount of tetrachlorobis(triphenylphosphine)rhenium(IV), $ReCl_4[(C_6H_5)_3P]_2$, was increased but never became the major product.

When excess triphenylphosphine was added to oxotrichlorobis(triphenylphosphine)rhenium(V) and ethanol-free chloroform, the major products were dichloromethyltriphenylphosphonium pentachlorotriphenylphosphineoxiderhenate(IV), $[(C_6H_5)_3PCHCl_2][ReCl_5(C_6H_5)_3PO]$, together with the chloride salt of the cation. When ethanol was present in the chloroform, the only isolated product was bis(methyltriphenylphosphonium) hexachlororhenate(IV), $[(C_6H_5)_3PCH_3]_2ReCl_6$. Addition of other alcohols to ethanol-free chloroform resulted in the formation of the same complex.

EXPERIMENTAL

INFRARED SPECTRA

Spectra of compounds were obtained over the range from 4,000 cm^{-1} to 250 cm^{-1} on a Model 521 Perkin-Elmer Grating Spectrophotometer. Except when expanded scales were desired, the spectrophotometer was operated in the normal scan mode. When expanded scales were desired, the abscissa was set at the linear scan with 2X or 5X expansion as described in the instrument manual. The ordinate was expanded from 2X to 5X as determined by the sample and described in the instrument manual. Scanning speed was reduced to 8 X 10, the slit program was reduced to 700 X 1, a gain of 4, and an attenuator speed of 1200 was used.

Potassium bromide disks were prepared by mixing 1.5 to 2.5 milligrams of sample with 150 milligrams of vacuum-dried potassium bromide. The mixture was finely ground in an agate mortar and pressed with 15,000 pounds pressure (total load) using a Perkin-Elmer evacuable die and a Carver Model B laboratory press.

Mulled samples were prepared using nujol. The nujol was dried by refluxing over phosphorus pentoxide for six hours in an evacuated flask. It was then distilled into a clean, evacuated flask and stored in the glove box. In cases where moisture-sensitive samples were used, the mull was prepared in the glove box.

Experiments were performed to determine the best way to protect the mull from reaction with moisture. A mull was prepared and sealed

between two polyethylene sheets. This sealed envelope was placed between cesium bromide plates to obtain a uniform thickness of the mull and the spectrum was obtained. After eight hours the same sample mull was rescanned. No change in the spectrum was observed. This was taken as evidence that no interaction with moisture was taking place. Another mull was prepared and placed directly between cesium bromide plates. This was removed from the glove box, put in a desiccator and taken to the instrument. The instrument had been purged with dry nitrogen for at least two hours before the spectrum was taken. The spectrum was identical with that observed when the sample was sealed between polyethylene. A second scan of the same sample mull was taken two hours later with no observable change in the spectrum. This was taken as evidence that no interaction with moisture was taking place. Subsequent sample mulls were supported between cesium bromide plates without sealing in a polyethylene sandwich.

MASS SPECTRA

Mass-spectral data were obtained at South Dakota State University using a Finnegan Gas Chromatograph Peak Identifier Model 3000 equipped with a solid probe and probe heater. A glass separator was used at the interface of the Varian Model 1429-1 gas chromatograph and the mass spectrometer. Helium was used as the carrier gas. The column used was either glass or stainless steel, five-feet in length and one-eighth inch in diameter packed with 3% OV-1 on 60/80 GCQ.

Some mass-spectral data were obtained by Dr. David Nelson at the University of Wyoming using a Varian CH-5 High Resolution Mass Spectrometer.

ELECTRONIC SPECTRA

Electronic spectra were recorded in solution using a Beckman DK-2A Ratio Recording Spectrophotometer and one-centimeter silica cells.

MOLECULAR MASS

Molecular mass determinations were made using a Mechrolab Vapor Pressure Osmometer Model 301A operated at a temperature of 37°C.

NUCLEAR MAGNETIC RESONANCE SPECTRA

Nuclear magnetic resonance data were obtained with a Varian A60-A Spectrometer with the probe maintained at ambient temperature.

X-RAY PHOTOGRAPHS

X-ray diffraction photographs of powdered samples were recorded using a Picker Model 681400 Debeye-Scherrer camera with a diameter of 114.6 millimeters and nickel filtered CuKα radiation from a Picker Nuclear Model 6147 x-ray instrument. Films were read using a Norelco x-ray film reader. Intensities were visually estimated.

RHENIUM ANALYSES

Rhenium analyses were made either gravimetrically, using 0.1 to 0.2 gram samples, by precipitation of tetraphenylarsine perrhenate according to the method of Willard and Smith (48), or colorimetrically,

using 10 to 30 milligram samples, by a modification of the method of Meloche et al. (49).

Samples which could not be prepared for analysis by treatment with aqueous sodium hydroxide and 30% hydrogen peroxide required treatment in a Parr sodium peroxide bomb and were analyzed colorimetrically. Because the fusion reaction in the peroxide bomb did not completely oxidize the sample of triphenylphosphine complexes it became necessary to construct a standard curve using known triphenylphosphine complexes. The standard curve was constructed from the known amount of rhenium in each sample and the absorbance, as measured at 532 nanometers. A concentration-versus-absorbance graph was constructed, which obeyed Beers Law up to at least 2.25 micrograms of rhenium per milliliter. The resulting graph was used to determine the concentration of rhenium in the solution being analyzed. The rhenium content of the compound being analyzed was found from the concentration.

CHLORINE ANALYSES

Chlorine analyses were carried out gravimetrically according to the fusion method of Niederl and Niederl (50).

OTHER ANALYSES

Carbon, hydrogen and phosphorus analyses were performed by Galbraith Laboratories of Knoxville, Tennessee.

RHENIUM METAL

Rhenium metal powder was used as obtained from Shattuck Chemical Company.

AMMONIUM PERRHENATE

Ammonium perrhenate was used as received from Shattuck Chemical Company.

TRIPHENYLPHOSPHINE

Triphenylphosphine was used as received from M and T Chemicals, Inc.

OXOTRICHLOROBIS(TRIPHENYLPHOSPHINE)RHENIUM(V)

Oxotrichlorobis(triphenylphosphine)rhenium(V) was prepared according to the method of Leitheiser (47). The infrared spectrum of oxotrichlorobis(triphenylphosphine)rhenium(V), was identical to the spectrum of a reference sample of the compound, as shown in Figure 13, page 160.

Analysis: Theoretical for $ReOCl_3C_{36}H_{30}P_2$: Re 22.35%; Cl 12.77%; C 51.99%; H 3.61%. Found: Re 22.61%; Cl 13.21%; C 51.25%; H 3.48%.

SOLVENT PURIFICATION

All solvents underwent a preliminary treatment by appropriate methods (51)(52) to remove impurities, followed by drying over calcium sulfate or molecular sieves to remove most of the water. Final purification was carried out in the apparatus shown in Figure 2. The apparatus was rinsed with portions of the solvent to be purified, then flushed for one hour with nitrogen which was dried by passage through granular phosphorus pentoxide. The drying agent and a magnetic

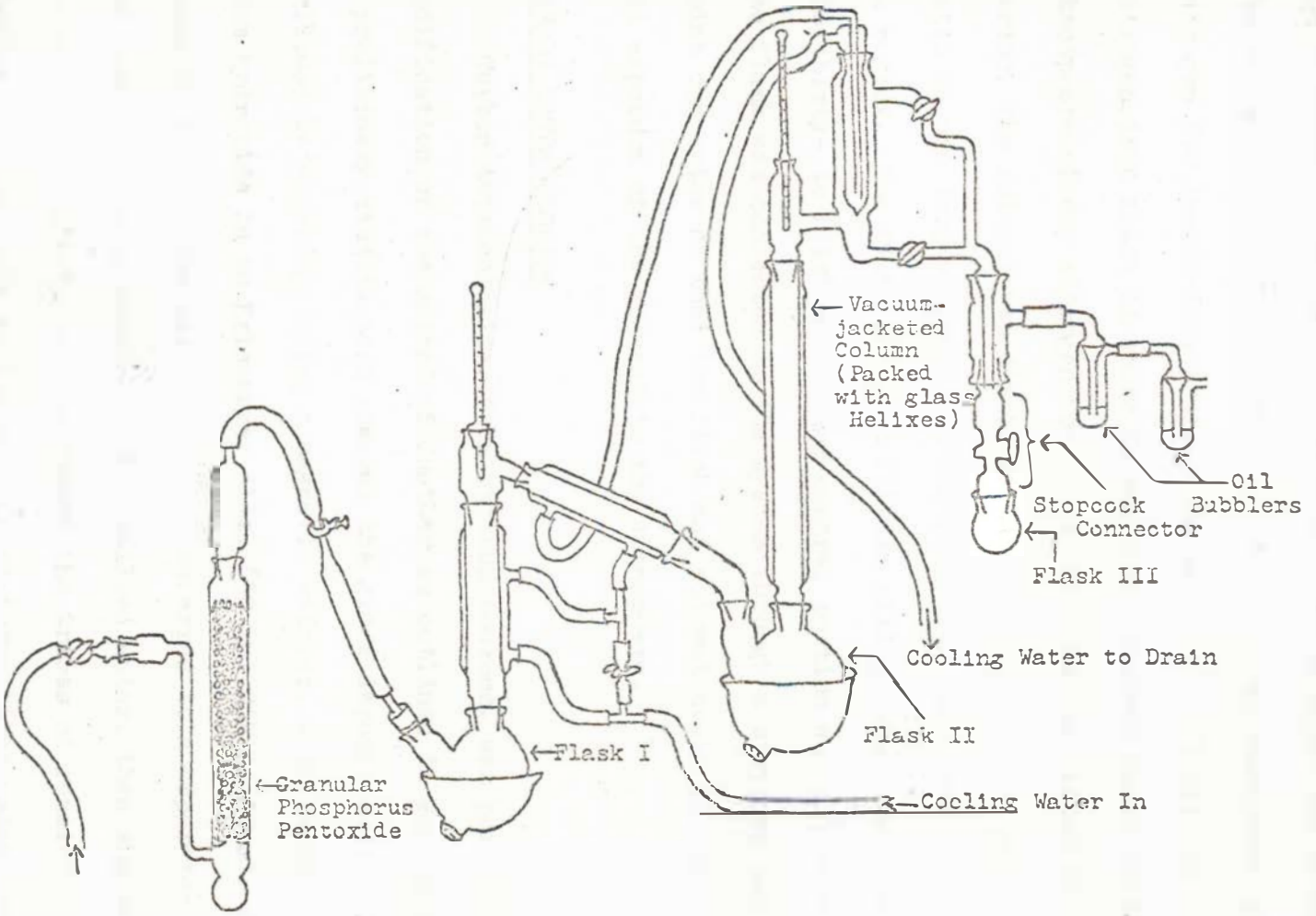


Figure 2

Solvent Purification Apparatus

stirring bar were placed in flasks I and II. After drying, the solvent was filtered to remove any preliminary drying agent and poured into flask I where it was stirred under reflux in an atmosphere of dry nitrogen for twenty-four hours. The solvent was distilled under nitrogen into flask II where it was again stirred under reflux in an atmosphere of dry nitrogen for twenty-four hours. After this reflux period, the solvent was distilled into a clean, dry flask at a reflux ratio of one drop collected in the flask for each five drops returned to reflux. The first and last fifteen milliliters were discarded and the thirty- to fifty-milliliter central portion was collected for use. The flask was connected to the system through a stopcock and ground joint connector so that the flask and solvent could be removed without exposure of the solvent to the atmosphere.

CARBON TETRACHLORIDE

Carbon tetrachloride, from various sources, was purified by a modification of the method of Gunther as outlined in Weissberger (51). A preliminary distillation removed the gross impurities. This was followed by stirring, using a magnetic stirrer, with alcoholic potassium hydroxide in an Erlenmeyer flask (30 gm. KOH in 50 ml. water added to 50 ml. ethanol). It was transferred to a separatory funnel and washed twice by shaking with distilled water, then shaken with concentrated sulfuric acid to remove the traces of remaining ethanol. Shaking with sulfuric acid was repeated three times using fresh sulfuric acid each time. It was washed by shaking with five or six

portions of distilled water until the water layer was neutral to litmus. Most of the residual water was removed by stirring with calcium sulfate for six hours. Phosphorus pentoxide was used in the previously described final purification.

CHLOROFORM

Chloroform, obtained from various sources, was purified by modifying the method of Budde as outlined in Weissberger (51). Chloroform was shaken vigorously for five minutes with about thirty milliliters of concentrated sulfuric acid followed by drawing the sulfuric acid out of the separatory funnel. This procedure was repeated four times with fresh portions of concentrated sulfuric acid. After the sulfuric acid treatment, the solvent was washed with distilled water. These washings were continued with fresh portions of water until the wash water was neutral to litmus. Most of the residual water was removed by drying over calcium sulfate for six hours. Phosphorus pentoxide was used in the previously described final purification.

CYCLOHEXANE

Cyclohexane, obtained from various sources was treated according to the method of Crowe and Smyth as outlined in Weissberger (51). After washing to remove the nitric acid and sulfuric acid, the cyclohexane was dried overnight by storing over calcium sulfate. Fresh sodium wire was used in the final purification described previously.

ACETONE

Acetone (Reagent grade) was obtained from various sources. A preliminary drying step was performed by storing over anhydrous calcium sulfate or molecular sieves for twenty-four hours. It was then filtered onto fresh anhydrous calcium sulfate and final purification was carried out as described previously.

1,4-DIOXANE

Dioxane was obtained from Matheson, Coleman and Bell as "Spectrograde" reagent. This was purified by storing over sodium wire for twenty-four hours. It was then transferred to the distillation apparatus where final purification from fresh sodium was carried out as described previously.

DIETHYL ETHER

Diethyl ether was obtained from Mallinkrodt as Absolute ether. This was purified by storing over sodium wire and distilling from fresh sodium in the distillation apparatus as described previously.

2-BUTANONE

The 2-butanone was obtained from Matheson, Coleman and Bell, and was used as received.

ALUMINUM OXIDE

Rhenium complexes have been found (53) to decompose on chromatography columns of other than acidic aluminum oxide (alumina). The aluminum oxide, obtained from J. T. Baker Chemical Company, was placed

in a separatory funnel and concentrated hydrochloric acid was added to it and shaken. These washings were continued with fresh portions of concentrated hydrochloric acid until the hydrochloric acid no longer became yellow upon shaking with the aluminum oxide. The aluminum oxide was then shaken with portions of distilled water until the pH of the water portion was about three. The water was removed and the aluminum oxide dried at 250° C for three days. It was then stored in an oven at 120° C.

RHENIUM(V) CHLORIDE

Rhenium(V) chloride was prepared from metallic rhenium and anhydrous chlorine according to the procedure described by Gehrke (54). Rhenium(V) chloride was present in the sausage tubes as a dense "plug" following vacuum sublimation. This "plug" could sometimes be broken away from the wall of the tube by hitting the outside of the tube with a heavy rubber stopper mounted on a rod. Frequently, this treatment was not successful, so the sausage tube was opened in the glove box and the rhenium(V) chloride was broken up with a large glass rod and a spatula. After rhenium(V) chloride was removed from the sausage tubes, it was stored under vacuum, in sealed vials (10 mm. x 5 cm.). The apparatus shown in Figure 3 was used in the following manner. The entire apparatus was attached to the manifold of the high vacuum system and evacuated to 5×10^{-5} torr. The stopcock was closed and the apparatus was transferred to the glove box, disassembled and a sample of about 1.00 gram of rhenium(V) chloride was placed in the lower part of the apparatus. The apparatus was

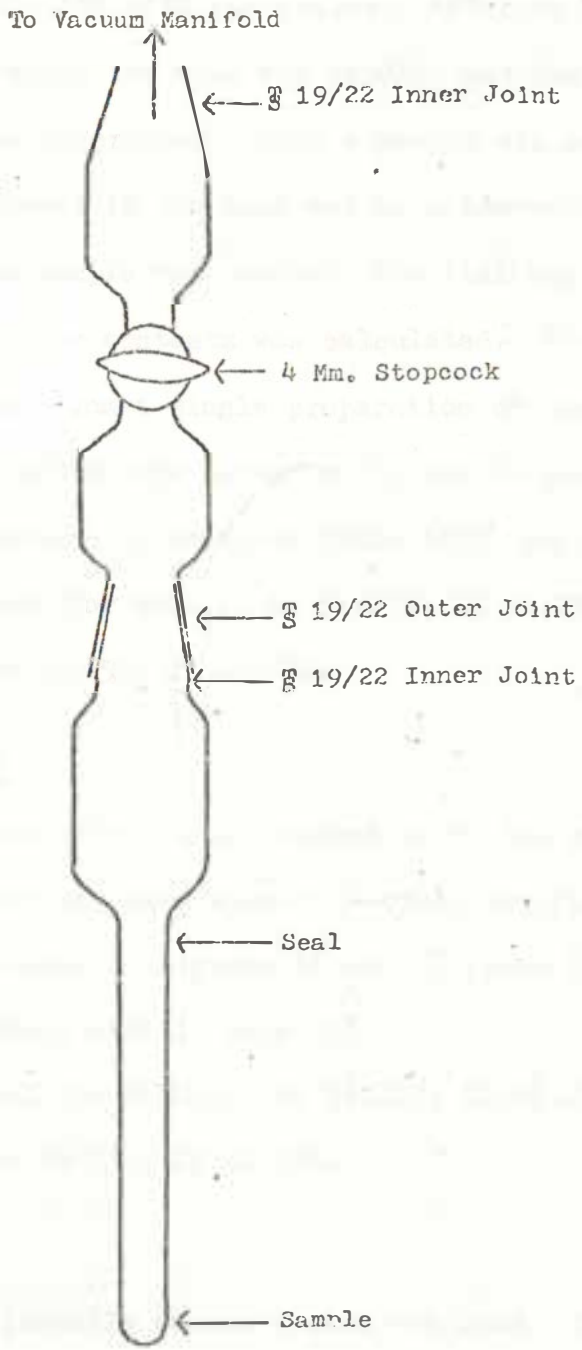


Figure 3

Vials for Storing Rhenium(V) Chloride

reassembled and returned to the vacuum manifold. The pressure was reduced to 5×10^{-5} torr and the vial was sealed. After it had been sealed and the seal was cool, the vial was labeled and the mass of the vial and its contents was determined. When a sample was needed for a reaction, the vial was opened in the same way as a piece of glass tubing is cut. After the sample was removed, the vial and label were reweighed and the mass of the contents was calculated. Twenty to thirty vials were obtained from a single preparation of rhenium(V) chloride. The infrared spectra are shown in Figures 14 and 15, page 160. The x-ray powder pattern is shown in Table XXII, page 79.

Analysis: Theoretical for $ReCl_5$: Re 51.23%; Cl 48.77%.
Found: Re 51.5%; Cl 48.67%.

OXOTETRACHLORORHENIUM(VI)

The oxotetrachlororhenium(VI) was prepared by D. Bue at South Dakota State University and was used without further purification. The infrared spectra are shown in Figures 16 and 17, page 161. The x-ray data are shown in Table XXVIII, page 155.

Analysis: Theoretical for $ReOCl_4$: Re 54.10%; Cl 41.22%.
Found: Re 54.05%; Cl 41.59%.

VACUUM SYSTEM

A Delmar Scientific portable vacuum system was used. This system was modified for solution experiments by adding a nitrogen inlet to the vacuum manifold (see Figure 4). Nitrogen was admitted to the vacuum manifold through a tube containing BTS catalyst heated

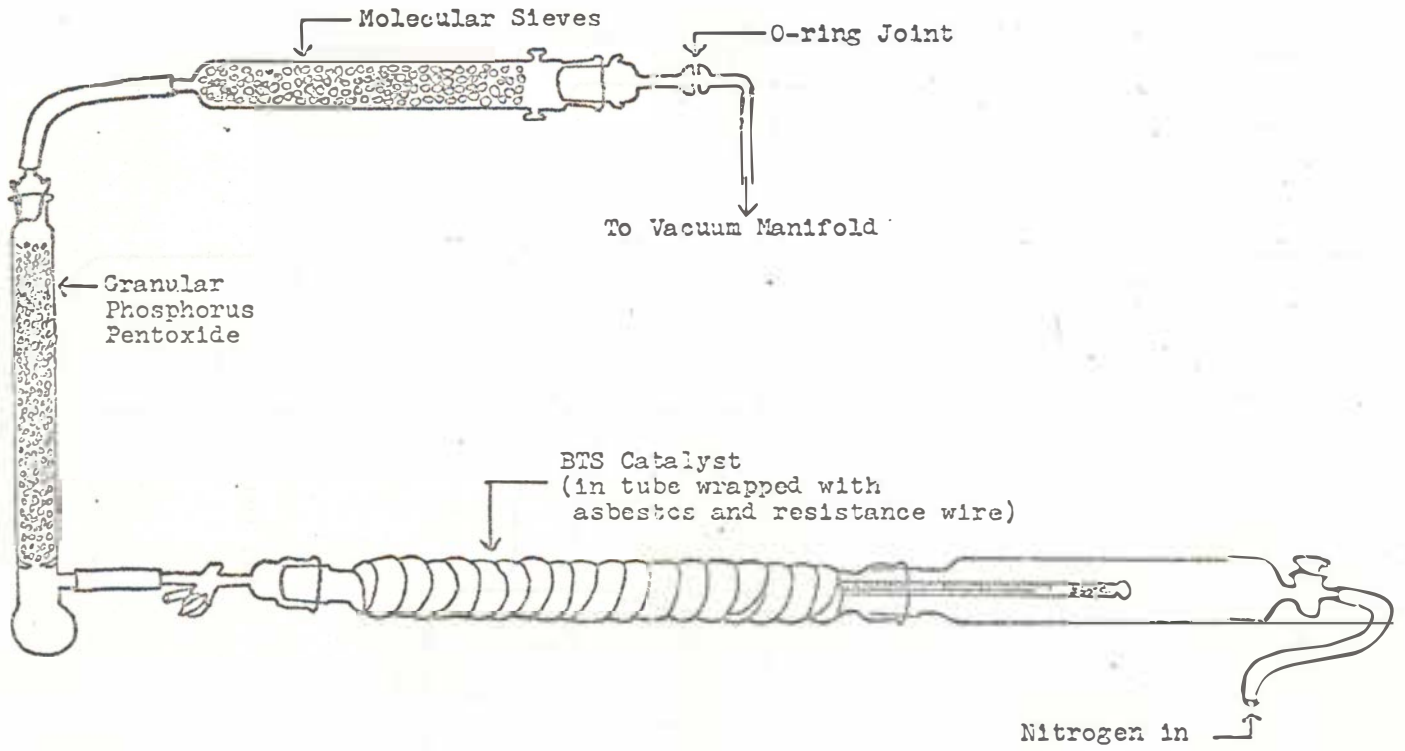


Figure 4

Nitrogen Purification System

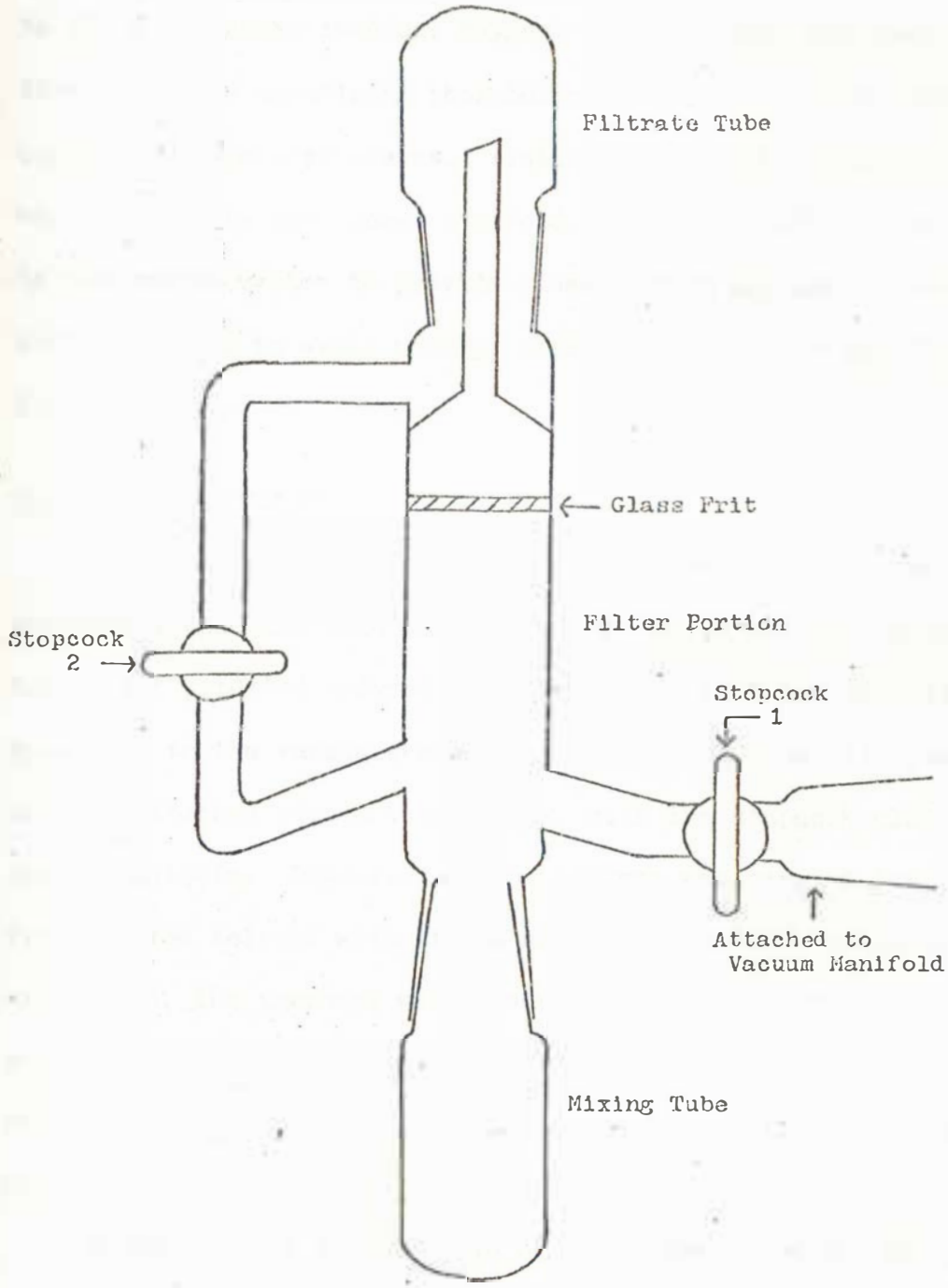


Figure 5

Vacuum-line Filtration Apparatus.

to 200°C to remove residual oxygen. The nitrogen was then passed through a tube containing phosphorus pentoxide and then through a tube containing molecular sieves. Finally, the purified and dried nitrogen was admitted to the vacuum manifold. A second modification was made to the vacuum system to provide a means of bypassing the mercury diffusion pump to avoid passing excess quantities of gas through the diffusion pump.

SOLUTION EXPERIMENTS

The experiments which involved the search for a solvent for rhenium(V) chloride were carried out on the vacuum system at 5×10^{-5} torr. The predried solvent was transferred from the distillation apparatus to the vacuum system by transferring flask III (see Figure 2) and the attached stopcock connector, with the stopcock closed, to the vacuum manifold. Degassing of the solvent was carried out by first freezing the solvent with liquid nitrogen. Second, while the solvent was frozen, the pressure was reduced to 5×10^{-5} torr. Third, the solvent was isolated from the vacuum system, by closing the stopcock on the stopcock connector, and the solvent was returned to the liquid phase. This freeze-pump-thaw cycle was repeated three times.

Meanwhile, the mass of each of the three parts of the apparatus, shown in Figure 5: the mixing tube, the filter portion, and the filtrate tube, was determined. Each part was equipped with sealed caps as required. After transferring the parts to the glove box again, a sample of rhenium(V) chloride was placed in the mixing tube. The mixing tube, containing the sample, and cap was removed from the glove box and the mass

was determined. It was then returned to the glove box and the three parts were assembled and removed from the glove box. The assembly was attached to the vacuum system, evacuated to a pressure of 5×10^{-5} torr, and tested for leakage. Leak testing was performed by isolating the manifold from the diffusion pump and noting, with the McCloed gauge, any changes in pressure. A system free of leaks was assumed if the pressure did not rise above 10^{-4} torr within one hour. If the system was found to be free of leaks, the liquid solvent was distilled from the storage flask onto the sample of rhenium(V) chloride. The distillation was accomplished by maintaining the mixing tube at the temperature of liquid nitrogen.

Following the transfer of the solvent into the mixing tube the apparatus was isolated from the vacuum manifold at stopcock 1 in Figure 5 and the solvent was liquified. When the solvent was at about room temperature, the mixture was stirred magnetically. After the mixture had been stirred for about one hour the apparatus was inverted by pivoting around the ground joint attached to the vacuum manifold (see Figure 5). This poured the mixture onto the sintered glass frit. Filtration was accomplished by closing stopcock 2 (Figure 5) and cooling the filtrate tube (Figure 5), thus creating a reduced pressure causing the solution to be drawn through the glass frit.

Any solid which was retained by the glass frit was washed by distilling portions of the solvent into the mixing tube by opening stopcock 2 and cooling the mixing tube with solid carbon dioxide. The

distilled solvent ran down onto the glass frit and was then drawn through the solid by again closing stopcock 2 and cooling the filtrate tube. This procedure was repeated until the solvent passing through the solid was no longer colored.

Following the washing of the solid, the solvent was removed from the solution by distillation into a flask. This was accomplished by maintaining the flask at the temperature of liquid nitrogen. When the solvent had been removed from the filtrate tube, the apparatus was filled with dry nitrogen and removed to the glove box. The apparatus was separated into its three parts and the mass of each part with its cap(s) was determined. The three parts were returned to the glove box where samples of the solid on the filter and the solid recovered from the solvent were prepared for analysis.

SCHLENK TUBES

Schlenk tubes similar to those described by Schlenk and Thal (55) (see Figure 6) were constructed by the glass blower at South Dakota State University. The design of the tubes was modified by the use of Teflon stopcocks and of Teflon sleeves on the standard-taper joints. The use of Teflon eliminated the need to use any grease. Associated with the use of Schlenk tubes is a buffer gas apparatus which makes possible the production and maintenance of an appropriate atmosphere in the Schlenk tubes. The buffer gas apparatus used in these experiments was constructed in the glass shop at South Dakota State University according to the design described by Herzog et al. (56). Figure 7 shows the system used.

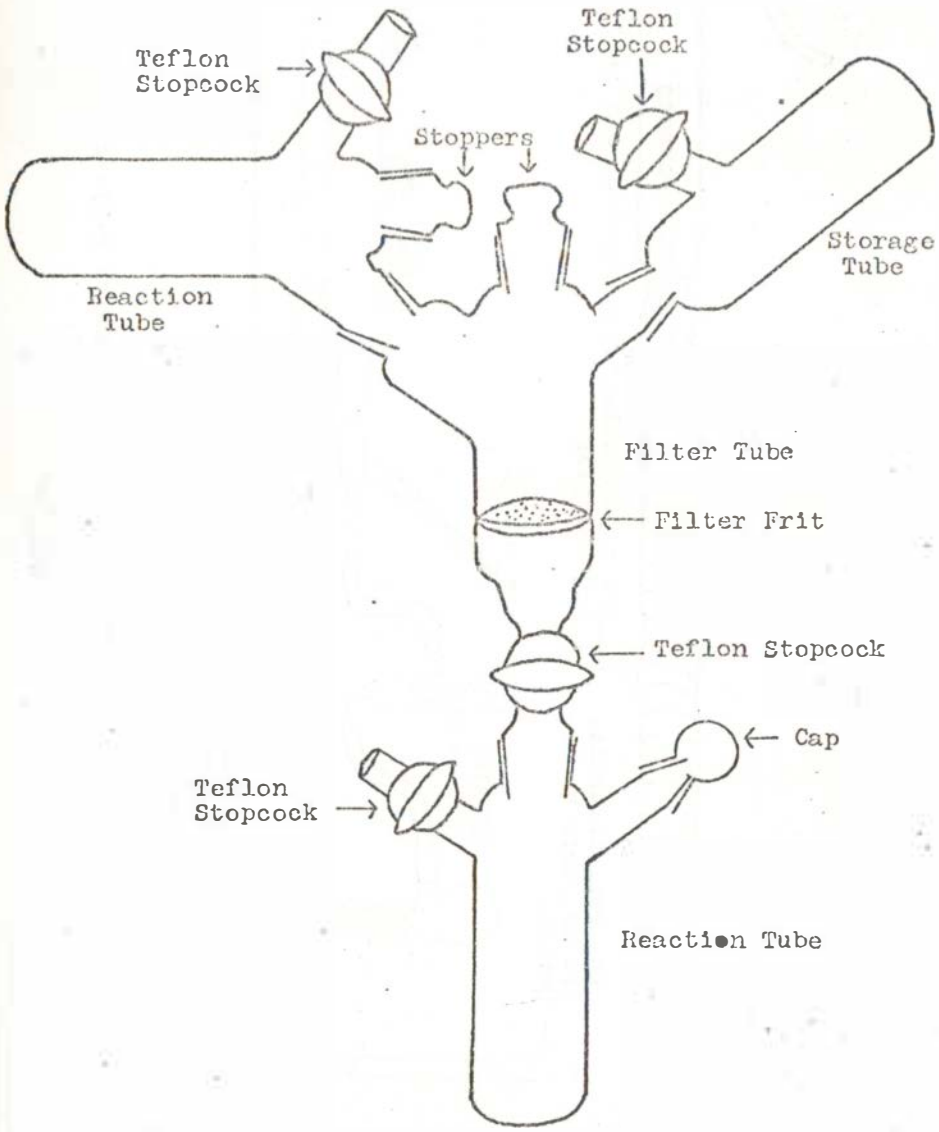


Figure 6

Examples of Schlenk Tube Apparatus

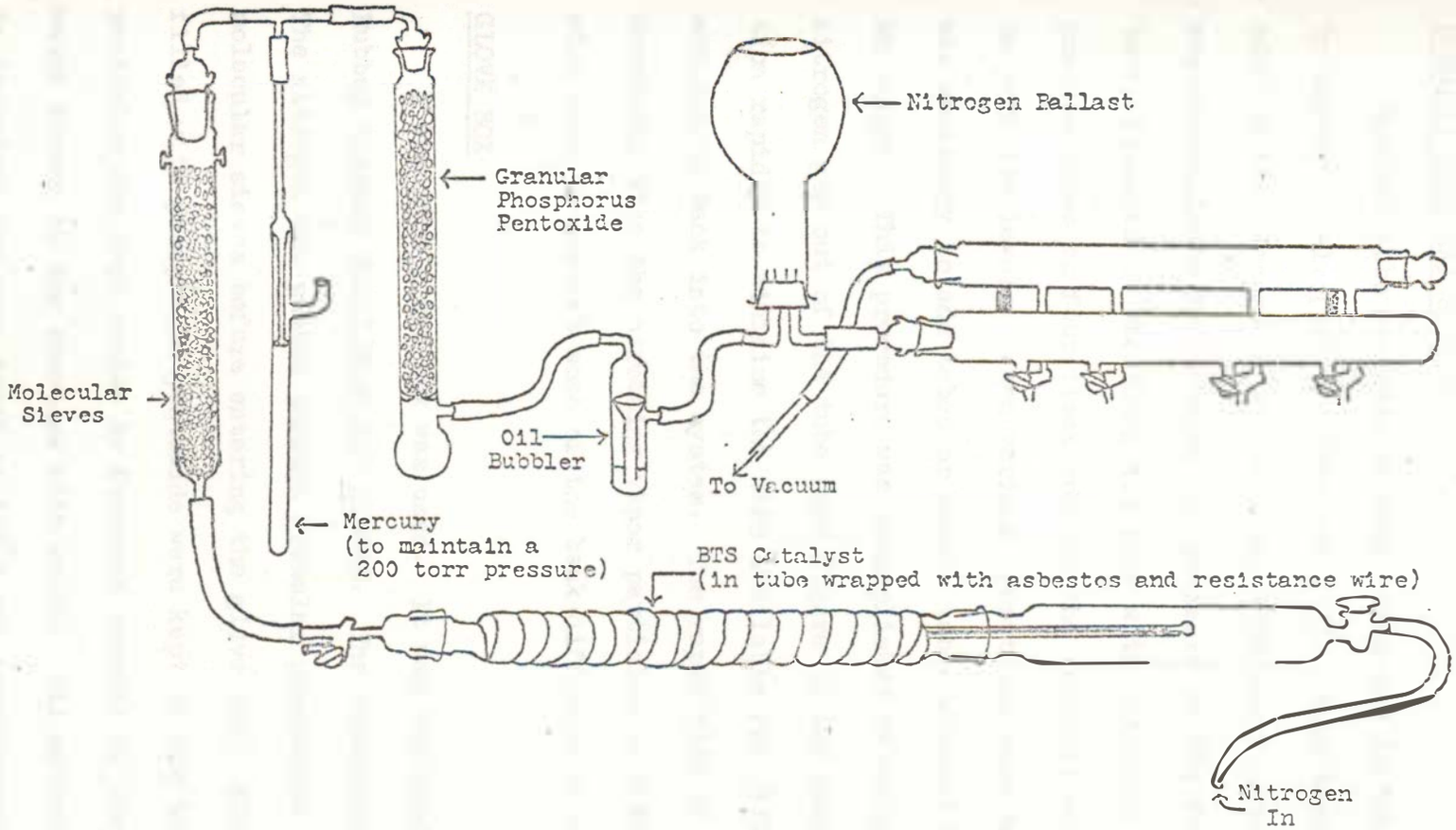


Figure 7

Buffer Gas Apparatus

SCHLENK TUBE EXPERIMENTS

Schlenk tube experiments were conducted in the manner outlined by Herzog et al. (56) and Schriver (57). This technique depends on replacing the atmosphere in the tubes with a dry nitrogen atmosphere. This was accomplished by lowering the pressure in the tube to less than one torr, followed by refilling the tube with nitrogen. Repeating this process three or four times reduced the residual moisture and oxygen to very low levels. When various operations were to be performed it was necessary to add tubes or remove tubes without introducing moisture or oxygen. This procedure was accomplished by using a rapid flow of nitrogen gas out of the tube (see Figure 8) and changing the connection rapidly to minimize the time available for diffusion of moisture and oxygen back into the system. The rapid flow of nitrogen acts something like the streaming vapor particles in a high-vacuum diffusion pump to prevent some of the back-diffusion of oxygen and moisture.

GLOVE BOX

A Hamilton glove box was used. It was equipped with Charleston Rubber Company Butyl Dura Sol gloves. The atmosphere was nitrogen. The nitrogen was passed through granular phosphorus pentoxide and molecular sieves before entering the glove box. Eight petri dishes filled with phosphorus pentoxide were kept in the box. The phosphorus pentoxide was kept active by frequent removal of the syrupy layer which formed by the reaction with water. All materials to be used in the glove box were dried at 120°C and transferred into the glove

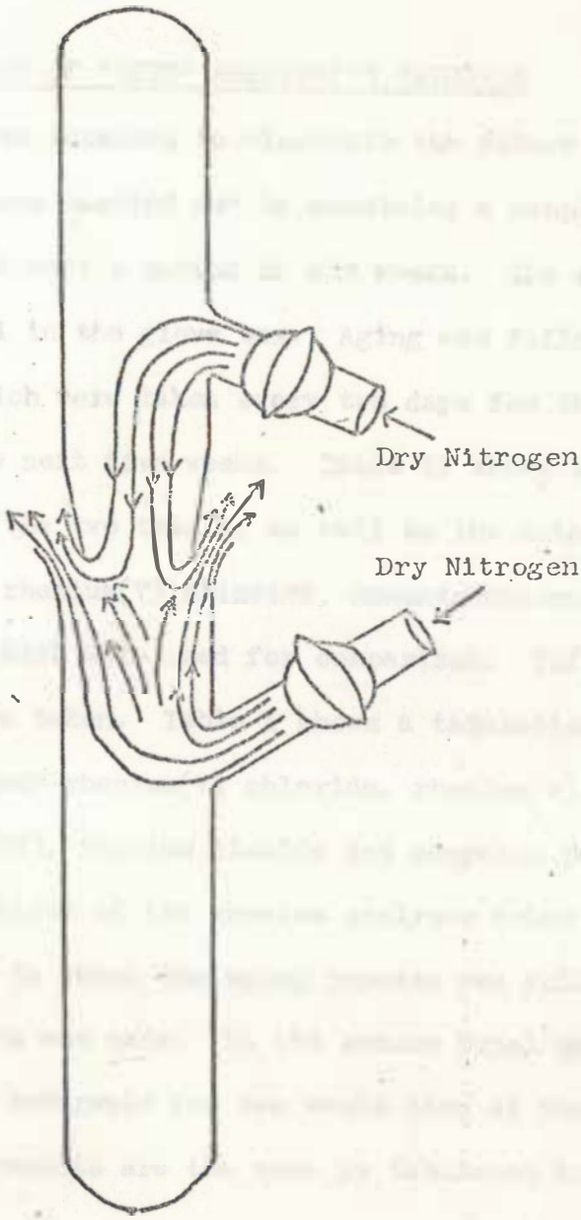


Figure 8

Path of Gas Flow in Schlenk Tube Apparatus

box through the entry port. The box was thoroughly cleaned at least once a year.

STUDIES INTO THE NATURE OF "AGED" RHENIUM(V) CHLORIDE

Studies which were intended to elucidate the nature of "aged" rhenium(V) chloride were carried out by examining a sample of rhenium(V) chloride as it changed over a period of six weeks. The sample was placed in an open vial in the glove box. Aging was followed by x-ray powder photographs which were taken every two days for the first week, then each week for the next five weeks. Table IX shows a tabulation of the results of one of the two trials, as well as the data for x-ray powder photographs of rhenium(V) chloride, oxotetrachlororhenium(VI), and rhenium dioxide, which were used for comparison. Infrared spectra, of the same sample were taken. Table X shows a tabulation of the bands observed for "aged" rhenium(V) chloride, rhenium(V) chloride, oxotetrachlororhenium(VI), rhenium dioxide and ammonium perrhenate. Table XI shows a tabulation of the rhenium analyses found during the study. A second trial in which the aging process was followed with x-ray powder photographs was made. In the second trial photographs were taken at one-week intervals for two weeks then at the end of the six-week period. The results are the same as tabulated in Table IX.

VACUUM LINE EXPERIMENTS WITH RHENIUM(V) CHLORIDE

Carbon Tetrachloride

Rhenium(V) chloride and carbon tetrachloride (ca. 20 ml.) were brought together in the mixing tube of the apparatus (see Figure 4).

TABLE IX

d-SPACINGS FROM X-RAY DATA DURING THE AGING OF RHENIUM(V) CHLORIDE COMPARED TO OTHER KNOWN COMPOUNDS

Sample Number (Intensity in Parentheses)

1	2	3	4	5	6	7	8	9	10
8.5(10)	8.4 (10)		8.6 (20)	8.7 (20)					
6.6(10)	6.5 (20)		6.6 (30)	6.7 (10)					
5.6(90)	5.6 (100)	5.6 (100)	5.6 (100)	5.6 (100)	5.6 (50)				5.4 (50)
5.1(80)	5.0 (90)	5.0 (90)	5.1 (100)	5.1 (90)	5.1 (100)	5.1 (100)	5.1 (100)		
4.7(30)			4.7 (30)	4.7 (40)	4.7 (20)	4.8 (10)	4.8 (10)		
4.1(30)	4.0 (30)		4.0 (40)	4.1 (30)			4.1 (10)		
3.7(40)	3.7 (10)		3.7 (20)	3.7 (20)					3.8 (100)
3.5(40)	3.5 (30)		3.5 (40)	3.5 (50)			3.42(10)	3.44(100)	3.56(80)
3.3(40)			3.3 (20)	3.2 (40)					
2.7(80)	2.64(90)	2.65(80)	2.66(70)	2.66(70)	2.66(40)	2.7 (20)	2.7 (10)		2.65(70)
2.6(40)	2.55(50)		2.56(40)	2.57(30)		2.6 (40)	2.6 (10)	2.56(50)	
2.4(70)	2.4 (80)	2.4 (70)	2.4 (70)	2.4 (80)	2.4 (60)	2.46(10)			2.39(50)
2.1(60)	2.1 (90)	2.1 (70)	2.1 (70)	2.1 (80)	2.1 (60)	2.19(10)		2.16(60)	
1.7(70)	1.7 (90)	1.7 (80)	1.7 (90)	1.7 (90)	1.82(50)	1.99(5)			
					1.77(40)			1.78(70)	
					1.74(40)				

Sample: 1) Rhenium(V) chloride and initial sample; 2) 2 days; 3) 4 days; 4) 6 days; 5) 10 days; 6) 21 days; 7) 27 days; 8) 44 days; 9) rhenium dioxide; 10) oxotetrachlororhenium(VI).

TABLE X

TABULATED INFRARED SPECTRA OF "AGED"
RHENIUM(V) CHLORIDE COMPARED TO OTHER KNOWN COMPOUNDS

Sample					
"AGED" $ReCl_5$ (cm^{-1})	Re_2Cl_{10} (cm^{-1})	$ReOCl_4$ (cm^{-1})	ReO_2 (cm^{-1})	NH_4ReO_4 (cm^{-1})	ReO_3Cl (cm^{-1})
1024	1036	1036			1001
915	910	913	912	915	
845		845			
420	423	419			435
400	400	400			
	396				
		388			
381	379	380			
375	374				
366	363				
	353	351			
348	348				
		340			
333	334				
	326				
320	321	322			
310	313	313			
		292			293
		283			
		269			
		255			

TABLE XI

RHENIUM ANALYSIS DURING
AGING OF RHENIUM(V) CHLORIDE

AGE OF SAMPLE (weeks)	PERCENT RHENIUM
0	51.5
1	54.6
2	57.2
3	61.5
6	69.2

Stirring was begun and within five minutes the solution became a very dark green. After stirring for one hour, the solution was filtered by inverting the apparatus, the solid retained on the filter was washed in the manner described previously. After the solid had been washed the solvent was distilled out of the filtrate tube and into a clean dry flask which had been attached to the vacuum manifold. During one of the experiments, the vacuum filtration apparatus was removed from the vacuum manifold before the solvent was distilled out of the filtrate tube and was transferred to the glove box and a sample of the solution was removed for an electronic spectrum. This spectrum showed an intense absorption maximum at 420 nanometers. Table XII shows the results of three experiments.

TABLE XII

RESULTS OF CARBON TETRACHLORIDE SOLUTION EXPERIMENTS

Re_2Cl_{10} used (grams)	Solid collected on filter (grams)	Recovered solute (grams)
0.77 (stirred 1 hour)	0.92	0.05
0.44 (stirred 1 hour)	0.65	0.09
1.24 (stirred 12 hours)	1.04	0.06

Analysis by x-ray-powder photography, infrared spectroscopy, and melting-point determination of the solid collected on the filter indicated that it was rhenium(V) chloride.

Analysis by x-ray-powder photography, infrared spectroscopy, and melting-point determination of the recovered solute showed that

it was not rhenium(V) chloride. The x-ray data are shown in Table XXXI, page 158. The infrared spectrum is shown in Figure 24, page 163.

Although the temperature of the silicon oil bath was raised to about 350° C, melting of the recovered solute was not observed. After the melting point tube had cooled, changes were observed in the solid in the tube. It appeared to have become more crystalline and it was red in color. An x-ray powder pattern was obtained as well as an infrared spectrum. These showed that it was rhenium(III) chloride. Elemental analysis was not made because of insufficient sample. The material dissolved in acetone produced a red solution. To this solution was added triphenylphosphine. After about two hours red crystals were observed. These were collected by filtration on sintered glass, washed with acetone and diethyl ether and dried. The infrared spectrum of these crystals showed that they were d-trichloro-(triphenylphosphine)rhenium(III). This reaction is peculiar to rhenium(III) chloride (54). The infrared spectrum of the rhenium(III) chloride which was removed from the melting point tube is shown in Figure 20, page 162. The x-ray data are shown in Table XXIX, page 156.

Carbon tetrachloride removed from the solute was subjected to gas chromatographic analysis and the eluted sample analyzed by mass spectrometry. This analysis showed that there were no new species present in the carbon tetrachloride.

Chloroform

Rhenium(V) chloride and chloroform (ca. 20 ml.) were brought together in the mixing tube of the apparatus (Figure 4). Stirring

was begun and within five minutes the solution became a very dark green. After stirring for one hour, the solution was filtered by inverting the apparatus. The solid retained on the filter was washed in the manner described previously. After the solid had been washed the solvent was distilled out of the filtrate tube and into a clean, dry flask which had been attached to the vacuum manifold. Table XIII shows the results of the experiment. Further work with the solvent, chloroform, was not carried out because of the very small amount of material which dissolved.

TABLE XIII

RESULTS OF CHLOROFORM SOLUTION EXPERIMENT

Re_2Cl_{10} used (grams)	Solid collected on filter (grams)	Recovered solute (grams)
0.61	0.57	0.03

Analysis by x-ray-powder photography, infrared spectroscopy, and melting-point determination of the solid collected on the filter showed that it was rhenium(V) chloride.

Analysis of the recovered solute was performed in the same mammer as described in the carbon tetrachloride trials and gave the same results.

Chloroform removed from the solute was subjected to gas chromatographic analysis and the eluted sample analyzed by mass spectroscopy. This analysis suggested the presence of a small quantity of tetrachloroethylene. Comparison of the mass spectrum of a known

sample of tetrachloroethylene showed that it was present in the chloroform removed from the solute.

Cyclohexane

Rhenium(V) chloride and cyclohexane (ca. 20 ml) were brought together in the mixing tube of the apparatus (Figure 4). Stirring was begun and within five minutes the solution became a very dark green. After stirring for one hour, the solution was filtered by inverting the apparatus. The solid retained on the filter was washed as described previously. An infrared spectrum of the cyclohexane solution after filtering showed only a band at 302 cm^{-1} which could be distinguished from the absorption bands due to the solvent. An electronic spectrum of the same solution showed one intense absorption centered at about 408 nanometers and a broad, very weak absorption at 625 nanometers.

After the solid had been washed, the solvent was transferred to a clean, dry flask. Gas chromatographic analysis indicated that there were no new species present in the cyclohexane after the reaction was completed.

Table XIV shows the data for one experiment. Further work with the solvent, cyclohexane, was not carried out because of the very small amount of material which dissolved.

Analysis by infrared spectroscopy of the solid collected on the filter suggested that it was "aged" rhenium(V) chloride. An analysis for rhenium and chlorine gave inconclusive results.

TABLE XIV

RESULTS OF CYCLOHEXANE EXPERIMENT

Re_2Cl_{10} used (grams)	Solid collected on filter (grams)	Recovered solute (grams)
0.99	0.57	0.03

Analysis of the recovered solute was frustrated because the oily material would not form a nujol mull and could not be placed in a melting point tube.

1,4-dioxane

Rhenium(V) chloride and 1,4-dioxane (ca. 20 ml.) were brought together in the mixing tube of the apparatus (Figure 4). Stirring was begun and within five minutes the solution was a very dark green. After stirring for one hour, the solution was filtered by inverting the apparatus. A gray solid was retained on the filter. Washing the solid turned it a pale green. The solid dissolved in acetone and an electronic spectrum was obtained in acetone solution. The spectrum contained absorption bands at 613, 648, 708 and 789 nanometers. The electronic spectrum together with the infrared spectrum (Figure 25, page 164) identified the compound as tetrachlorobis(1,4-dioxane)-rhenium(IV). When the solid was removed from the glove box, it was found that it was air sensitive. Table XV shows the results of this experiment. No further work was done with 1,4-dioxane because it did not appear to fit the criteria which were desired for a solvent for rhenium(V) chloride.

TABLE XV

RESULTS OF 1,4-DIOXANE EXPERIMENT

Re_2Cl_{10} used (grams)	Solid collected on filter (grams)	Recovered from solution (grams)
0.84	1.17	0.51

Diethyl ether

Rhenium(V) chloride and diethyl ether (ca. 20 ml.) were brought together in the mixing tube of the apparatus (Figure 4). Stirring was begun and within five minutes the solution was a deep reddish brown. After stirring for one hour, the solution was filtered by inverting the apparatus. A brown solid was retained in the filter. The solid was washed as described previously. After the solid was washed the solvent was transferred to a clean, dry flask. An infrared spectrum of the solid was obtained and is shown in Figure 26, page 164. When the material was removed from the glove box, it became oily and underwent a color change from brown to gray.

Analyses of the material recovered from the solution were frustrated by the intractable nature of the material. An attempt was made to prepare a nujol mull of the material, but it would not combine with nujol. Attempts to recrystallize the material from acetone resulted in decomposition of the material as indicated by a change in the color of the solid recovered from brown to gray. The solid which was recovered was not crystalline. Results of the solution experiment are shown in Table XVI.

TABLE XVI

RESULTS OF DIETHYL ETHER EXPERIMENT

Re_2Cl_5 used (grams)	Solid collected on filter (grams)	Recovered from solution (grams)
0.40	0.30	0.21

Acetone

Rhenium(V) chloride and acetone (ca. 20 ml.) were brought together in the mixing tube of the apparatus (Figure 4). Stirring was begun and within two minutes the solution became a very dark green. After stirring for one hour, the solution was filtered by inverting the apparatus. After washing, there was no solid remaining on the filter. When washing was completed it was found that the transfer of the solvent from the solution to a clean, dry flask took place very slowly and, even after five hours, was not complete. It was also observed that the pressure in the system was much higher (ca. 30 torr) than it should have been. This indicated that a leak was present and would account for the slow rate of transfer. Table XVII shows the results of this experiment. Further work with this solvent was not attempted because of the intractable nature of the material which was recovered from the solution.

Attempts to obtain an infrared spectrum were not successful because, instead of forming a mull, the product formed a glassy material on the bottom of the mortar. A spectrum of a saturated acetone solution of the recovered solute was obtained. The only

TABLE XVII

RESULTS OF ACETONE EXPERIMENT

Re_2Cl_{10} used (grams)	Solid collected on filter (grams)	Recovered from solution (grams)
0.89	0.00	2.04

absorption bands which were observed were those of the solvent, acetone. An electronic spectrum was obtained which showed an absorption maximum at 327 nanometers. Attempts to recrystallize the material from acetone and dimethylsulfoxide gave only the oil. The material was insoluble in methylene chloride. Gas chromatographic examination of the acetone used revealed no new species which could be separated by this technique.

Oxotetrachlororhenium(VI) and Carbon Tetrachloride

Oxotetrachlororhenium(VI) and carbon tetrachloride (ca. 20 ml.) were brought together in the mixing tube of the apparatus (Figure 4). Stirring was begun and within one minute the solution became a very dark green. After stirring for one hour, the solution was filtered by inverting the apparatus. There was no solid retained on the filter. An electronic spectrum of the solution was obtained. Absorption bands were observed at 785, 575 and 420 nanometers. After the sample for the electronic spectrum was removed, the solvent was transferred to a clean, dry flask. Table XVIII shows the results of this experiment.

Analysis by infrared spectroscopy of the material recovered from the solution showed that it was oxotetrachlororhenium(VI). When

TABLE XVIII

RESULTS OF OXOTETRACHLORORHENIUM(VI)
AND CARBON TETRACHLORIDE
EXPERIMENT

Mass of $ReOCl_4$ (grams)	Mass of solid retained on filter (grams)	Mass of material recovered from solution (grams)
0.36	0.00	0.34

placed in a sealed melting point tube, most of the material melted at about 30°C. The precise melting point was difficult to determine because the melting point tube was seemingly coated with the sample. Some of the material in the melting point tube did not melt even at 350°C.

Analysis: Theoretical for $ReOCl_4$: Re 54.14%; Cl 41.21%.

Found: Re 54.59%; Cl 41.51%.

Gas chromatographic analysis of the solvent removed from the solution revealed only the presence of carbon tetrachloride.

SCHLENK TUBE EXPERIMENTS WITH RHENIUM(V) CHLORIDE AND CARBON TETRACHLORIDE

Rhenium(V) chloride (1.38 gm., 3.80 mmol.) was transferred to a reaction tube in the glove box. After it was removed from the glove box the mass of the tube and the rhenium(V) chloride was determined. A solvent tube containing carbon tetrachloride was attached rapidly to the reaction tube under a rapid flow of dry nitrogen and the carbon tetrachloride was transferred to the reaction tube. The

resulting mixture was stirred with a magnetic stirrer for twenty-four hours. At the end of this time a filtration tube was attached under a rapid flow of dry nitrogen, and the mixture was filtered. The filter tube was detached under a rapid flow of nitrogen and its mass was determined. The amount of material in the filter tube and the reaction tube was found to be 1.33 grams. This material was shown to be rhenium(V) chloride by melting point determination, x-ray powder photography and infrared spectroscopy.

The tube which contained the solution was attached under a rapid flow of dry nitrogen to a reaction tube containing triphenylphosphine (1.00 gm., 3.82 mmol.). When the solution was poured onto the triphenylphosphine, a precipitate was immediately formed. The precipitate (0.12 gm., 0.14 mmol., 3.7% yield) was collected by filtration on sintered glass, washed with acetone to remove excess triphenylphosphine and dried. Tetrachloro(triphenylphosphinetriphenylphosphine oxide)rhenium(IV) was recrystallized from methylene chloride. The infrared spectrum is shown in Figure 27, page 164.

Analysis: Theoretical for $ReCl_4C_{36}H_{30}P_2O$: Re 21.43%; Cl 16.32%; P 7.13%; C 49.78%; H 3.48%. Found: Re 21.62%; Cl 16.46%; P 6.16%; C 50.11%; H 3.50%.

SCHLENK TUBE EXPERIMENTS WITH OXOTETRACHLORORHENIUM(VI) AND CARBON TETRACHLORIDE

Tetrachloro(triphenylphosphinetriphenylphosphine oxide)rhenium (IV), was prepared in Schlenk tubes from oxotetrachlororhenium(VI) (2.02 gm., 5.87 mmol.) and carbon tetrachloride (50 ml.). After

stirring for one hour, the mixture was filtered. No residue was left on the filter frit. Triphenylphosphine (5.00 gm., 19.08 mmol.) was added to the solution. The resulting precipitate was collected by filtration on sintered glass, washed with acetone and dried, giving an 83% yield (4.30 grams, 4.95 mmol.) of the pale green tetrachloro-(triphenylphosphinetriphenylphosphine oxide)rhenium(IV). It was recrystallized from methylene chloride. The infrared spectrum was identical to the one found for the reaction between rhenium(V) chloride and carbon tetrachloride with triphenylphosphine added (Figure 27, page 164).

Analysis: Theoretical for $ReCl_4C_{36}H_{30}P_2O$: Re 21.43%; C 49.78%; H 3.48%. Found: Re 21.28%; C 49.54%; H 3.52%.

REACTION OF RHENIUM(V) CHLORIDE IN ACETONE WITH EXCESS PYRIDINE

In the glove box, rhenium(V) chloride (1.0 gm., 2.75 mmol.) was dissolved in unpurified acetone (30 ml.), resulting in a very dark green solution. The flask was removed from the glove box and pyridine (15 ml., 185 mmol.) was added. The solution turned a very dark brown and a green precipitate was formed. The green solid was isolated by filtration, washed with acetone and dried. The green precipitate turned gray-green after it was removed from the solution. The mother liquor was set aside for two weeks. Orange crystals were isolated by filtration, washed with acetone and diethyl ether and dried, giving 0.39 gram (0.64 mmol., 23% yield) dioxotetrakis(pyridine)rhenium chloride dihydrate. It was recrystallized from methylene chloride. The infrared spectrum is shown in Figure 28, page 165.

Analysis: Theoretical for $ReO_4ClC_{20}H_{24}N_4$: Re 30.72%; Cl 5.85%; C 39.63%; H 3.99%. Found: Re 30.55%; Cl 6.05%; C 39.57%; H 3.99%.

REACTION OF RHENIUM(V) CHLORIDE IN ACETONE WITH THE STOICHIOMETRIC AMOUNT OF PYRIDINE

In the glove box, rhenium(V) chloride (0.90 gm., 2.48 mmol.) was dissolved in unpurified acetone (13.5 ml.) producing a green solution. Pyridine (0.67 ml., 8.30 mmol.) was added to the acetone solution from a syringe. Some white "smoke" was observed while the solution remained green and a black precipitate formed. The precipitate was removed by filtration and the filtrate was removed from the glove box and placed in a desiccator. The black precipitate, which turned gray-green, was also removed from the glove box. The filtrate was examined after about an hour and some green crystals were observed. Two days later, the green crystals (0.16 gm., 0.19 mmol., 15% yield) were separated from the mother liquor by filtration, washed with acetone and diethyl ether and dried. The green crystals were recrystallized from methylene chloride-diethyl ether. The infrared spectrum of μ-oxodioxotetrachlorotetrakis(pyridine)dirhenium(V) is shown in Figure 29, page 165.

Analysis: Theoretical for $Re_2Cl_4O_3C_{20}H_{20}N_4$: Re 42.38%; C 27.97%; H 2.35%. Found: Re 42.25%; C 27.38%; H 2.35%.

REACTION OF "AGED" RHENIUM(V) CHLORIDE IN ACETONE WITH THE STOICHIOMETRIC AMOUNT OF PYRIDINE

In the glove box, "aged" rhenium(V) chloride (0.75 gm., 2.06 mmol.) was dissolved in unpurified acetone (11.2 ml.) producing a green solution. Pyridine (0.56 ml., 6.94 mmol.) was added from a syringe, resulting in a considerable volume of white "smoke" while the solution remained green. A green precipitate was also formed. Vacuum filtration in the glove box resulted in the collection of a gray-green precipitate, which turned black. After removing from the glove box, the precipitate was washed with acetone and dried, and it turned a gray-green color again. The filtrate was returned to the flask and within five minutes green crystals began to form. The flask was removed from the glove box and placed in a desiccator. After sitting for twenty-four hours, the green solid was isolated by filtration on sintered glass, washed with acetone and diethyl ether and dried, giving a 23% yield (0.20 gm., 0.23 mmol.) of crude product. The green crystals were recrystallized from methylene chloride-diethyl ether. The infrared spectrum was identical to that of μ-oxodioxotetrachlorotetrakis(pyridine)dirhenium(V), (Figure 29, page 165), which was produced in the reaction of fresh rhenium(V) chloride in acetone with pyridine, as discussed previously.

The gray-green solid, which formed soon after pyridine was added to the acetone solution and was collected within five minutes of the addition of pyridine, contains some organic material, as indicated by the fact that it burns. Qualitative analysis indicated that the

solid contains a small amount of rhenium and a large amount of chloride. It does not dissolve in methylene chloride or water. Addition of aqueous sodium hydroxide caused the formation of black rhenium dioxide which was oxidized to the perrhenate ion upon the addition of 30% hydrogen peroxide. The infrared spectrum is shown in Figure 30, page 165. No further work was carried out in an attempt to identify the gray-green solid.

REACTION OF RHENIUM(V) CHLORIDE WITH ACETIC ACID

Rhenium(V) chloride (0.68 gm., 1.84 mmol.) was placed in a dry, 100 milliliter three-necked flask in the glove box. The flask was removed from the glove box and a dry nitrogen inlet tube was attached under a rapid stream of dry nitrogen. A reflux condenser fitted with a calcium sulfate drying tube was attached to the flask under a stream of dry nitrogen. Acetic acid (25 ml.), to which had been added acetic anhydride (5 ml.), was added to the rhenium(V) chloride through the reflux condenser against a stream of dry nitrogen. The solution which was black was refluxed for forty-eight hours in an atmosphere of dry nitrogen. During this period of time the solution remained black and a black solid deposited on the flask at the surface of the solution.

After two days the acetic acid was evaporated off by passing dry nitrogen over it without heating. The solid was removed from the flask and chloroform was added. A black solution with some black solid was formed. The black solid (0.20 gm.) was removed by filtration. A second black solid was formed upon reducing the volume of the

chloroform solution. Both black solids gave the same infrared spectrum (Figure 31, page 166). Neither black solid ignited in a flame, indicating the absence of organic material.

Analysis: Found: Re 64.63%; Cl 1.62%.

SEALED TUBE REACTIONS

Reactions of oxotrichlorobis(triphenylphosphine)rhenium(V) in sealed tubes were carried out in a tube fifteen millimeters in diameter and twenty-one centimeters in length (see Figure 9). The

Figure 9

Tube Used for Sealed Tube Experiments

constriction near the top facilitates sealing the tube. The tube held about eighteen milliliters of solvent. When sealing the tube, the glass was heated at the constriction until soft enough to draw out. This caused the glass to become thinner and also smaller in diameter. The flame was made much hotter and a seal was quickly made. The seal was cooled and tested for leaks by bathing the inside of the seal with the solvent. A leak was detected if any solution was forced out of the tube. An iron pipe four centimeters in

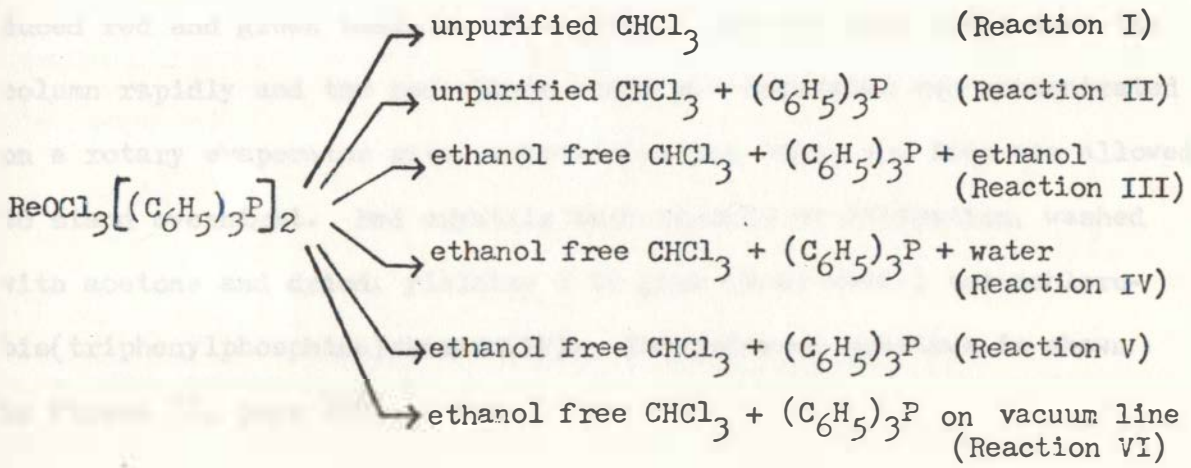
diameter and twenty-two centimeters in length, with a screw cap at each end, was used as a safety container in the event that the tube would explode. The tube was placed in a thermostatically controlled oven for from five to twenty-four hours. After it was removed from the oven it was allowed to cool to room temperature. Prior to opening the tube, it was placed in an ice bath to reduce any pressure which may have built up in the tube. To open the tube, a scratch was made near the constriction and a crack was produced by touching the scratch with a hot glass rod.

SEALED TUBE REACTIONS OF OXOTRICHLOROBIS(TRIPHENYLPHOSPHINE)RHENIUM(V) WITH CHLOROFORM

Several reactions with chloroform and oxotrichlorobis(triphenylphosphine)rhenium(V) were carried out. The varying conditions of the chloroform are summarized in Table XIX.

TABLE XIX

CHLOROFORM USED IN SEALED TUBE REACTIONS



Reaction I

Oxotrichlorobis(triphenylphosphine)rhenium(V) (0.37 gm., 0.44 mmol.) was placed in a reaction tube together with chloroform (15 ml., 186 mmol.). The mixture was heated to boiling to remove dissolved gases and the tube was sealed and placed in an oven at 120°C for seventeen hours. The tube was removed from the oven and cooled. It was found to contain a pale-green solid and a red-brown solution. After opening the tube the green solid (0.26 gm., 0.29 mmol.) was separated from the solution by filtration, washed with five milliliters of chloroform and dried. It was recrystallized from chloroform. The infrared spectrum of tetrachlorobis(triphenylphosphine oxide)-rhenium(IV) is shown in Figure 32, page 166.

Analysis: Theoretical for $ReCl_4C_{36}H_{30}P_2O_2$: Re 21.05%; Cl 16.04%; C 48.88%; H 3.42%. Found: Re 21.12%; Cl 16.52%; C 48.65%; H 3.99%.

The red-brown mother liquor was concentrated to about eight milliliters and passed down an acid-washed alumina column. This produced red and green bands on the column. The red band moved down the column rapidly and the red eluate which was collected was concentrated on a rotary evaporator until crystallization began and then was allowed to stand overnight. Red crystals were removed by filtration, washed with acetone and dried, yielding 0.02 gram (0.02 mmol.) tetrachlorobis(triphenylphosphine)rhenium(IV). The infrared spectrum is shown in Figure 33, page 166.

Analysis: Theoretical for $ReCl_4C_{36}H_{30}P_2$: Re 21.84%; Cl 16.63%. Found: Re 21.30%; Cl 16.98%.

The green band moved down the column slowly. Concentration of the resulting green eluate produced a trace of green solid. The green solid was shown to be tetrachlorobis(triphenylphosphine oxide)rhenium (IV) by infrared spectroscopy.

Reaction II

Oxotrichlorobis(triphenylphosphine)rhenium(V) (0.52 gm., 0.62 mmol.) and triphenylphosphine (1.00 gm., 3.82 mmol.) were placed in a reaction tube together with unpurified chloroform (17 ml., 211 mmol.). The mixture was heated to boiling to remove dissolved gases. The tube was sealed and placed in an oven at 120°C for nineteen hours. The tube was removed and cooled. It was found to contain a pale-green needle-shaped solid in a red-brown solution. After opening the tube, the green solid (0.32 gm., 0.34 mmol.) was isolated by filtration on sintered glass, washed with cold chloroform and dried. It was recrystallized from methylene chloride. The infrared spectrum of bis-(methyltriphenylphosphonium) hexachlororhenate(IV) is shown in Figure 34, page 167.

Analysis: Theoretical for $ReCl_6C_{38}H_{36}P_2$: Re 19.53%; Cl 22.31%; C 47.86%; H 3.81%. Found: Re 19.52%; Cl 22.39%; C 47.71%; H 3.84%.

The red-brown mother liquor was concentrated to about eight milliliters, yielding additional bis(methyltriphenylphosphonium)

hexachlororhenate(IV) which was isolated by filtration on sintered glass, washed with cold chloroform and dried. The infrared spectrum was identical to that shown in Figure 34, page 167.

The concentrated mother liquor was passed down an alumina column producing a red band, which moved down the column very rapidly, and a green band. The resulting red eluate was concentrated to about ten milliliters. Crystallization was induced by adding five milliliters of diethyl ether, yielding, by filtration, a trace of red solid identified as tetrachlorobis(triphenylphosphine)rhenium(IV) by infrared spectroscopy.

The green band was eluted with methylene chloride, producing a pale-yellow-green eluate. Concentration of the eluate produced a trace of pale-green solid only when all of the solvent was removed. An infrared spectrum of the pale green solid showed that it was bis-(methyltriphenylphosphonium) hexachlororhenate(IV).

Reaction III

Oxotrichlorobis(triphenylphosphine)rhenium(V) (0.50 gm., 0.60 mmol.) and triphenylphosphine (1.00 gm., 3.82 mmol.) were placed in a reaction tube together with ethanol-free chloroform (17 ml., 211 mmol.) to which 0.25 milliliter (4.2 mmol.) of absolute ethanol had been added. The mixture was heated to boiling to remove dissolved gases. The tube was sealed and placed in an oven at 120°C for fifteen hours. The tube was removed from the oven and cooled. It was found to contain pale green needle-shaped crystals in a green solution. After opening the tube, the green solid (0.50 gm., 0.52 mmol.) was

isolated by filtration on sintered glass, washed with cold chloroform and dried. It was recrystallized from methylene chloride. The infrared spectrum of bis(methyltriphenylphosphonium) hexachlororhenate(IV) is shown in Figure 34, page 167.

Analysis: Theoretical for $ReCl_6C_{38}H_{36}P_2$: Re 19.53%; Cl 22.31%; C 47.86%; H 3.81%. Found: Re 19.38%; Cl 22.19%; C 47.65%; H 3.71%.

The green mother liquor was concentrated to about eight milliliters and passed down an alumina column producing only a green band. The resulting pale-green eluate was concentrated to about five milliliters, yielding a trace of bis(methyltriphenylphosphonium) hexachlororhenate(IV) which was collected by filtration, washed with cold chloroform and dried. It was identified as bis(methyltriphenylphosphonium) hexachlororhenate(IV) by infrared spectroscopy.

Reaction IV

Oxotrichlorobis(triphenylphosphine)rhenium(V) (0.50 gm., 0.60 mmol.) and triphenylphosphine (1.00 gm., 3.82 mmol.) were placed in a reaction tube together with ethanol-free chloroform to which 7.6 microliters (0.42 mmol.) of deionized water had been added. The mixture was heated to boiling to remove dissolved gases. The tube was sealed and placed in an oven at 120°C for fifteen hours. The tube was removed from the oven and cooled. It was found to contain a green crystalline solid and a reddish solution. After opening the tube, the green solid (0.43 gm.) was isolated by filtration on

sintered glass, washed with cold chloroform and dried. Attempts to recrystallize the green solid from methylene chloride, acetone and dimethylsulfoxide resulted in its decomposition as indicated by changes in the infrared spectrum. The infrared spectrum of the unrecrystallized-green solid is shown in Figure 35, page 167. The infrared spectrum of the green solid after attempted recrystallization from methylene chloride is shown in Figure 36, page 167.

Concentration of the mother liquor to about ten milliliters yielded less than 0.01 gm. of what appeared from the infrared spectrum to be the same material as was produced upon attempted recrystallization from methylene chloride. This product was not identified.

The concentrated mother liquor was passed down an alumina column producing a red band and a green band. The red band moved down the column rapidly, producing a red eluate which was concentrated to about ten milliliters. Crystallization was induced by adding five milliliters of diethyl ether. A red solid was collected and identified as tetrachlorobis(triphenylphosphine)rhenium(IV) by infrared spectroscopy.

The green fraction would not elute with acetone, methylene chloride, tetrahydrofuran, or dimethylsulfoxide.

Reaction V

Oxotrichlorobis(triphenylphosphine)rhenium(V) (0.50 gm., 0.60 mmol.) and triphenylphosphine (1.00 gm., 3.82 mmol.) were placed in a reaction tube together with ethanol-free chloroform (17 ml., 211

mmol.). The mixture was heated to boiling to remove dissolved gases. The tube was sealed and placed in an oven at 120°C for fifteen hours. The tube was removed from the oven and cooled. It was found to contain a mixture of green and brown crystals and a purple powder and a brown solution. After opening the tube, the mixture of solids (0.52 gm.) was isolated by filtration on sintered glass, washed with chloroform and dried. When the washings were added to the mother liquor a copious amount (0.84 gm.) of white powder was formed.

The purple powder was separated from the green and brown crystals by dissolving it in chloroform. The green and brown crystals were separated from the purple solution by filtration and washed with chloroform and dried. The purple solution was concentrated to about five milliliters and the purple powder which formed over a period of one week was collected by filtration of sintered glass, washed with five milliliters of cold chloroform and dried, yielding 0.03 gram. Recrystallization from chloroform resulted in the recovery of 0.01 gram of the purple powder. The infrared spectrum of the purple powder is shown in Figure 64, page 171. Analysis was possible only after collecting samples from several reactions.

Analysis: Found: Re 21.46%; Cl 18.56%; C 47.59%; H 3.35%.

No further work was possible with this material because of the limited quantities produced in the reaction.

The green and brown crystals dissolved in methylene chloride, but decomposed. Several attempts were made to cause rapid crystallization before decomposition occurred. Diethyl ether was added to the

solution in an attempt to induce crystallization, but decomposition still resulted. Vacuum evaporation of the solvent without heat was not rapid enough to prevent decomposition. When heat was applied, decomposition occurred more rapidly. The crystals were not soluble in other solvents. Partial separation of the green crystals from the brown crystals was achieved by mechanical separation under a magnifying lens. The infrared spectrum of dichloromethyl(triphenylphosphonium) pentachloro(triphenylphosphine oxide)rhenium(IV) is shown in Figure 47, page 171.

Analysis: Theoretical for $ReCl_7C_{37}H_{31}P_2O$: Re 18.85%; Cl 25.12%; P 6.27%; C 44.98%; H 3.16%. Found: Re 19.15%; Cl 25.62%; P 6.20%; C 44.25%; H 3.27%.

The brown, crystalline material was not analyzed because infrared spectroscopy indicated that it was an impure sample of the green crystals.

The white solid dissolves in ethanol and can be reprecipitated from ethanol without changes in the infrared spectrum. Considerable work was carried out with this solid in an attempt to identify it. Table XX summarizes the work which was carried out.

Formation of this white solid is reproducible under varying conditions. The white solid formed when filtration of the products of the sealed tube reaction was carried out on the laboratory bench, or if care was taken to exclude moisture by carrying out all operations in the glove box. This reproducibility was shown by comparison

TABLE XX

EXPERIMENTAL DATA RELATIVE TO THE NATURE OF
THE WHITE POWDER PRODUCED FROM THE MOTHER LIQUOR OF REACTION V

Sample	Data Collected
Crude material	10.89% ionic chlorine 24.47% total chlorine Mass spectrum indicates presence of chloroform Infrared spectrum Figure 37, page 168
Recrystallized material	10.80% ionic chlorine 11.41% total chlorine Mass spectrum indicates no chloroform Analysis C 67.37%; H 5.88% Infrared spectrum Figure 38, page 168
Recrystallized then heated at 80°C	10.38% total chlorine Mass spectrum indicates two chlorines in a molecular mass of 538 VPO molecular mass of 1.60 molal solution is 216; of 2.90 molal solution is 276 Analysis C 66.50%; H 5.61%; P 9.45% Infrared spectrum Figure 39, page 168
Reaction with $NH_4[Cr(NH_3)_2(SCN)_4]$	Analysis C 54.32%; H 4.31% Infrared spectrum Figure 41, page 169
Reaction with $Na(C_6H_5)_4B$	Infrared spectrum Figure 43, page 170
Reaction with NH_4ReO_4	Infrared spectrum Figure 45, page 170

of the infrared spectra of the white solid obtained in all trials of this reaction.

Reaction VI

To reduce to a minimum the water and oxygen present in Reaction V, a tube was fitted with a ground-glass joint and attached to the vacuum system. Seventeen milliliters of degassed ethanol-free chloroform (degassed by three freeze-pump-thaw cycles) were transferred to the reaction tube which contained oxotrichlorobis(triphenylphosphine)-rhenium(V) (0.33 gm., 0.42 mmol.) and triphenylphosphine (1.00 gm., 3.82 mmol.) under high vacuum (5×10^{-5} torr). The tube was sealed, allowed to warm to room temperature, and placed in an oven at 120° C for fifteen hours. It was removed from the oven and cooled. The tube was found to contain green and brown crystals, a purple powder and a brown solution. After opening the tube in the glove box, the mixture of solids (0.35 gm.) was separated from the solution by filtration on sintered glass, washed with purified chloroform and dried. When the washings were added to the solution, a white solid formed and was collected in the glove box by filtration on sintered glass, washed with chloroform and dried. The infrared spectrum of the white powder was identical with spectra of white powders formed in other trials of this reaction.

The green and brown crystals gave the same infrared spectrum as in previous trials. Similarly the purple powder gave the same infrared spectrum as in other trials.

SEALED TUBE REACTION OF OXOTRICHLOROBIS(TRIPHENYLPHOSPHINE)RHENIUM(V) WITH ACETONE

Oxotrichlorobis(triphenylphosphine)rhenium(V) (0.30 gm., 0.40 mmol.) was placed in a reaction tube together with acetone (13 ml.). The mixture was heated to boiling to remove dissolved gases. It was sealed and placed in an oven at 120°C for twenty-four hours. The tube was removed from the oven and cooled. It was found to contain a green solid and a brown solution. After opening the tube, the green solid (0.17 gm.) was isolated by filtration on sintered glass, washed with acetone and dried. The infrared spectrum of the isolated material indicated it was unreacted oxotrichlorobis(triphenylphosphine)rhenium (V).

The brown mother liquor from the reaction was concentrated to about eight milliliters and set aside for three weeks. No crystalline product formed. The solution was further concentrated to about five milliliters by slow evaporation at room temperature. An oil was produced. Efforts to form a nujol mull of the oil produced a glassy solid which adhered to the mortar and would not form a mull. The oil was redissolved in acetone, and diethyl ether was added in an attempt to induce crystallization. An oil was produced. No further work was carried out because of the intractable nature of the sample.

SEALED TUBE REACTION OF OXOTRICHLOROBIS(TRIPHENYLPHOSPHINE)RHENIUM(V) WITH 2-BUTANONE

Oxotrichlorobis(triphenylphosphine)rhenium(V) (0.50 gm., 0.60 mmol.) was placed in a reaction tube together with 2-butanone

(Matheson, Coleman and Bell). Contents of the tube were not boiled. The tube was sealed and placed in an oven at 120° C for twenty-four hours. The tube was removed from the oven and cooled. It was found to contain a green solid and a blue-green solution. After opening the tube, the green solid (0.12 gm.) was isolated by filtration on sintered glass, washed with chloroform and dried. The infrared spectrum of the isolated solid indicated that it was unreacted oxotrichlorobis(triphenylphosphine)rhenium(V).

The blue-green solution from the reaction was concentrated to about five milliliters and a blue-green solid was precipitated with the addition of twenty milliliters of hexane. This solid was dissolved in chloroform (10 ml.) and the solution was passed down an alumina column. Red, dark-blue, green, yellow, and pale-blue bands were observed on the column. The red band was eluted first, but evaporating the eluate produced insufficient solid to obtain an infrared spectrum. The dark-blue band eluted next and the eluate was concentrated on a rotary evaporator, without heat, to about ten milliliters. This concentrate was passed down a fresh alumina column; a blue and a green band were observed on the column. The blue band was eluted and the resulting eluate concentrated to about ten milliliters. Diethyl ether was added, resulting in the slow formation of a dark-blue solid. The dark-blue solid was isolated by filtration on sintered glass, washed with diethyl ether and dried. It was dissolved in chloroform (20 ml.), concentrated to ten milliliters and diethyl ether was again added resulting in the formation of the dark-blue

solid. This was repeated two more times, resulting in the formation of 0.12 gram of trichloro(triphenylphosphine oxide) rhenium(III). The infrared spectrum is shown in Figure 48, page 171.

Analysis: Theoretical for $ReCl_3(C_6H_5)_3PO$: Re 32.62%; Cl 18.72%.
Found: Re 32.18%; Cl 18.53%.

The green and yellow bands of the original alumina column moved down the column together. The forward fractions of the green band and the last fractions of the yellow band were collected. Evaporation of the combined fractions from the green band yielded a green solid. Evaporation of the combined fractions from the yellow band yielded a second green solid. The two green solids appeared, by visual inspection, to be the same. Infrared spectra of the two green solids were indistinguishable. The infrared spectrum of the green solid is shown in Figure 49, page 172.

The pale-blue band of the original alumina column remained at the top of the column until acetone was used as the solvent. The blue band then moved down the column rapidly and the resulting eluate was concentrated by evaporation. The blue solid formed had an infrared spectrum which was identical to that of trichloro(triphenylphosphine oxide)rhenium(III).

DISCUSSION

RHENIUM(V) CHLORIDE

The objective of this research was to gain insight into the solution chemistry of rhenium(V) chloride and from solutions, to obtain molecular mass data and evidence for nonequivalent chlorines which would lead to conclusions concerning the structure of rhenium(V) chloride. The research was also concerned with the preparation of cluster compounds of rhenium(V).

In order to accomplish these goals it was necessary to establish some reference points. These reference points were the properties of rhenium(V) chloride—its melting point, its infrared spectrum, its x-ray powder pattern and the formation of a solution without reaction.

The literature provided two melting point values: 220°C (5) and 260°C (2)(4)(58). Since there was such a large difference, it was necessary to re-examine this property. The infrared spectrum was reported in two studies (20)(21) and they were in substantial agreement with each other. Therefore, comparisons could be made to the reported spectra. The solid state structure of rhenium(V) chloride had been elucidated (11) by x-ray analysis of a single crystal. X-ray powder photographs were necessary.

Melting Point

The melting point of rhenium(V) chloride is important because of the formation of rhenium(IV) chloride which occurs at or slightly below the melting point of rhenium(V) chloride (23). Rhenium(IV)

chloride has been the object of curiosity and considerable research into its preparation (2) because of its unique cluster arrangement and also its elusive nature. Because of the instability of rhenium(V) chloride, all melting points were determined in sealed capillary tubes. Melting points of rhenium(V) chloride observed in this research were all between 260°C and 265°C. It is possible that early workers reported low melting points because of impure samples, improper apparatus or heating the sample too rapidly. All of these can cause an observed melting point to be lower than it actually is.

Because of the possibility of decomposition occurring while a melting point determination was made, the sample was examined by x-ray powder photography and infrared spectroscopy both before and after a melting point determination. If decomposition occured it was expected that rhenium(III) chloride and/or rhenium(IV) chloride would form, since these are products of the decomposition of rhenium(V) chloride. Neither of these species was observed in the infrared spectrum or in the x-ray powder photograph.

Infrared Spectra

Smardzewski (20) has reported the infrared spectrum of rhenium(V) chloride as a nujol mull and in cyclohexane. A normal coordinate analysis based on the x-ray structure (11) resulted in very good correlation between the observed and calculated absorption frequencies. Edwards and Ward (21) have reported a similar spectrum of rhenium(V) chloride.

Infrared spectra which have been obtained in the course of this work were substantially different than those reported. This difference is shown in Table XXI. In Table XXI the region which shows rhenium-chlorine absorptions (59) is considered. It will be observed that there is some similarity between the spectra. Each of the rhenium(V) chloride spectra show bands at 390 cm^{-1}, 350 cm^{-1} and 275 cm^{-1}. Note that when the spectrum of oxotetrachlororhenium(VI) is compared to the spectra of rhenium(V) chloride, the strongest absorptions occur at 388 cm^{-1} and 383 cm^{-1} in oxotetrachlororhenium(V) and these also appear in the spectra of rhenium(V) chloride. However, since the most intense absorption for the rhenium(V) chloride used in this research appeared at 350 cm^{-1} where no oxotetrachlororhenium(VI) absorption was observed, and since other less intense bands of oxotetrachlororhenium(VI) did not appear in the spectrum of the rhenium(V) chloride used in this work but did appear in the spectra reported by others (e.g. $ReOCl_4$; 402 cm^{-1}, 257 cm^{-1}, 255 cm^{-1}), it was concluded that the rhenium(V) chloride spectrum obtained in this research was more representative of rhenium(V) chloride than those obtained by others. Further evidence for the presence of oxotetrachlororhenium(VI) was found when the infrared region between 1100 cm^{-1} and 800 cm^{-1} was examined. This is the region in which absorptions due to rhenium-oxygen bonds occur (50). This examination revealed a small (ca. 3% above the base line) absorption band at 1036 cm^{-1} which is indicative of the rhenium-oxygen absorption of oxotetrachlororhenium(VI) (58)(59).

TABLE XXI

INFRARED SPECTRUM OF RHENIUM(V) CHLORIDE

Smardzewski (20)	Edwards and Ward (21)	This Work	$ReOCl_4$ (This Work)
		420 (w)	
404 (s)	402 (sh)		402 (sh)
393 (s, sh)		390 (m)	388 (vs)
	383 (s)		383 (vs)
		375 (s)	
369 (ms)		364 (s)	
350 (ms)	357 (s)	350 (vs)	
			340 (w)
		335 (sh)	
		328 (m)	
		324 (m)	
			320 (w)
		315 (w)	
			308 (w)
		301 (m)	
		299 (m)	
			290 (w)
		288 (w)	
			283 (w)
276 (m)		275 (m)	
			268 (m)
	257 (m)		257 (m)
255 (ms)			255 (ms)

vs = very strong; s = strong; ms = moderately strong;
m = moderate; w = weak; sh = shoulder

It is difficult to determine the extent of the impurity in rhenium (V) chloride. Some estimate can be made based on the infrared spectrum. An infrared spectrum of oxotetrachlororhenium(VI) and the band at 1036 cm^{-1} compared to the impurity band in the infrared spectrum of rhenium(V) chloride shows that the intensity of the impurity band was 8% of the intensity of the band in pure oxotetrachlororhenium(VI). Further information on the molar absorptivity of that band is required before a closer estimate of the amount of impurity can be made.

Elemental analysis of rhenium(V) chloride was considered satisfactory; it differed from the theoretical value by less than 0.5%. If there were 5% oxotetrachlororhenium(VI) in rhenium(V) chloride, the analysis for rhenium would be 51.4% rather than the theoretical 51.23%. The analysis was found to be 51.5%. Chlorine analysis would have been 48.4% instead of the theoretical 48.77%. It was found to be 48.67%. On the basis of these estimates, there might be about 5% impurity in the rhenium(V) chloride used in this research.

These observations caused an extensive effort to purify rhenium(V) chloride. First, consideration was given to the sources of oxygen and their effect on the formation of impurities in the preparation of rhenium(V) chloride. Since oxotetrachlororhenium(VI) is formed by the action of oxygen on rhenium(V) chloride at 180°C (58) and is not the result of hydrolysis at room temperature, it must be formed along with rhenium(V) chloride. Therefore, oxygen must be present in the reaction apparatus or be introduced into the reaction apparatus during the preparation of rhenium(V) chloride. Oxygen could come from the rhenium

metal which might contain oxides. This possibility seemed unlikely because any rhenium oxides should be reduced at 1000°C in a hydrogen atmosphere. A second source of oxygen might be the nitrogen gas used. This was possible, but since the sample was not heated in a nitrogen atmosphere, and the nitrogen was passed over activated copper (BTS catalyst) and through phosphorous pentoxide it was not likely that the oxotetrachlororhenium(VI) could be formed from oxygen or water in the nitrogen. Water which may be adsorbed on the glass surfaces could be a source of oxygen. This is unlikely because the glass was heated while evacuated to desorb the water. Furthermore water is not a source of oxygen for the formation of oxotetrachlororhenium(VI) because, in the presence of water, rhenium(V) chloride undergoes hydrolysis to form rhenium dioxide, perrhenic acid and hydrogen chloride (5). Another source of oxygen could be the chlorine gas used in the preparation of rhenium(V) chloride. Specifications (60) for Research Grade chlorine indicate that it contains less than 50 parts per million oxygen. Chlorine used to prepare the rhenium(V) chloride for this research was of lower purity, designated "High Purity" chlorine. Such lower grades might contain greater amounts of oxygen. Because no record was kept of the amount of chlorine used, it was not possible to say if this could account for the impurity noted in the rhenium(V) chloride. Guest and Lock (58) have considered the presence of oxygen in chlorine used for the preparation of rhenium(V) chloride and have used only degassed chlorine in their preparations of rhenium(V) chloride.

The purification of rhenium(V) chloride was carried out in a tube about 28 millimeters in diameter. This tube was constructed with constrictions about every 15 centimeters along the tube so that it appeared to be a series of sausages linked together. This appearance suggested the name, "sausage" tube. Rhenium(V) chloride was sublimed directly into the sausage tube after it passed out of the heated region of the tube where the rhenium and chlorine were combined. After all rhenium had reacted, the rhenium(V) chloride was sublimed twice in a flow of chlorine gas. The system was cooled, flushed with dry nitrogen and evacuated. The reaction tube and the first two sections of the sausage tube were removed by sealing under vacuum. Then the rhenium(V) chloride was slowly sublimed at 150°C into the next section of the sausage tube and again sealed. This was repeated a total of three times. Rhenium(V) chloride was sealed into the sausage tubes which remained. After this purification process the rhenium(V) chloride was removed from the sausage tube and stored in sealed vials. A sample was taken and an infrared spectrum obtained which still exhibited the band due to rhenium-oxygen at 1036 cm^{-1}.

Since the band was reduced in intensity by this purification procedure, but not removed, it was concluded that the impurity had been reduced to as low a level as possible and the research should continue.

X-Ray Analysis

To further insure that the sample used in this work was rhenium(V)

chloride and to obtain data which would be used later in studying the "aging" of rhenium(V) chloride the d- spacings of the powder photograph were compared with the d- spacings calculated from the single crystal data of Mucker et al.(11). Table XXII shows the results of this comparison. The d- spacings were calculated for the fifty reflections having the largest structure factor (F_{obs}). (61) The table also shows the intensities which were estimated visually on the powder photographs. These compare well with calculated intensities from the single crystal analysis. Intensities from the single crystal analysis were calculated from the Lorentz Polarization Factor (61) given by the expression $I = F_{hkl}^2\left(\frac{1 + \cos^2 2\theta}{\sin^2\theta\cos\theta}\right)$, where I is the intensity, F_{hkl} is the observed structure factor, θ is calculated from Bragg's law, $\sin\theta = \frac{\lambda}{2d}$, where λ is the wavelength of the x-ray beam and d is the interplanar spacing. The table shows good correlation between the powder data and the single crystal data. This further suggests that the rhenium(V) chloride sample which was used in this research had the same structure as that on which the crystal structure was determined. Lines which occur at 8.65 and 6.67 must be due to impurities. Comparison to powder patterns of rhenium(III) chloride, rhenium(IV) chloride and oxotetrachlororhenium(VI) show that there are some d- spacings which are close to those, but none which match well.

"AGED" RHENIUM(V) CHLORIDE

"Aged" rhenium(V) chloride has been found (8)(29) to react in a

TABLE XXII

COMPARISON OF CALCULATED AND OBSERVED
d- SPACINGS OF RHENIUM(V) CHLORIDE

Observed	Intensity	Calculated (11)	Intensity
8.65	(m)		
6.67	(s)		
5.69	(vs)	5.69	(100+)
5.19	(s)	5.14	(100)
4.45	(w)		
4.34	(m)		
4.17	(m)	4.18	(61)
3.95	(w)		
3.76	(w)	3.76	(23)
3.52	(m)	3.52	(30)
3.27	(m)	3.28	(27)
2.95	(m)	2.96	(27)
2.75	(w)	2.75	(10)
2.67	(s)	2.67	(63)
2.58	(m)	2.57	(14)
2.47	(mw)	2.47	(22)
2.40	(w)	2.37	(33)
2.08	(s)	2.08	(25)
1.99	(w)	1.96	(8)
1.89	(w)	1.88	(19)
1.84	(w)	1.83	(14)
1.74	(s)	1.74	(95)
1.70	(w)	1.70	(7)
1.64	(w)		
1.59	(vw)	1.58	(7)
1.56	(w)	1.55	(6)
1.51	(vw)	1.52	(12)
1.46	(vw)	1.46	(6)
1.43	(vw)	1.44	(9)
1.40	(vw)	1.40	(6)
1.34	(w)	1.33	(6)
1.31	(w)	1.32	(6)

vs = very strong; s = strong; m = moderate; w = weak; vw = very weak

different manner than does fresh rhenium(V) chloride. Cotton et al. (29) found that rhenium(V) chloride, when "aged", would react with excess pyridine to form μ-oxodioxotetrachlorotetrakis(pyridine)rhenium(V), $Re_2O_3Cl_4(C_5H_5N)_4$, and dioxotetrakis(pyridine)rhenium(V) chloride dihydrate, $\left[ReO_2(C_5H_5N)_4\right]Cl \cdot 2H_2O$, while fresh rhenium(V) chloride produced only an uncharacterized solid. Gehrke and Eastland (8) have found that "aged" rhenium(V) chloride affected the ratio of reaction products in the reaction of rhenium(V) chloride in acetone to which was added an acetone solution of triphenylphosphine. These products were described in Table VIII, page 15. They found that "aged" rhenium (V) chloride reacted in much the same way as did fresh rhenium(V) chloride when wet acetone was used as the solvent. It has been suggested (2) that the differences between fresh rhenium(V) chloride and "aged" rhenium(V) chloride are due to partial hydrolysis of rhenium(V) chloride. The work of Gehrke and Eastland was in agreement with the proposal that partial hydrolysis had occurred. This was suggested by their observation that the use of wet acetone and fresh rhenium(V) chloride lead to much the same result as did the use of "aged" rhenium(V) chloride. Still no conclusion had been reached as to the nature of this species. The present investigation set out to elucidate the nature of the "aged" species. Determining the nature of the "aged" species could help to explain why "aged" rhenium(V) chloride reacts in a different way than does fresh rhenium(V) chloride.

Rhenium(V) chloride was "aged" by placing it in an open vial and leaving it in the glove box. The "aging" process was followed by

x-ray photographs and analysis at intervals until no further changes were observed. Infrared spectra were also used to observe the process.

X-Ray Analysis

X-ray powder photographs were taken at intervals over a six-week period. The d- spacing was calculated, tabulated and compared to d- spacings of other materials which might be found in "aged" rhenium(V) chloride. These included rhenium dioxide, oxotetrachlororhenium(IV), rhenium(III) chloride and rhenium(IV) chloride. Two other samples which could be formed were not included. One of these was the perrhenate ion which was not included because it would be present as perrhenic acid which has not been isolated (5). The other species which was not included was trioxochlororhenium(V) because its melting point is 4.5° C, so if it were present, it would be present as a liquid and x-ray powder photographs would be impossible. The data which were collected were tabulated in Table IX on page 40. An examination of this table reveals that there were almost no changes in the measured d- spacings and estimated intensities during the first two weeks. Changes which did occur could have been caused by changes in the quality of sample preparation. Since each sample taken for x-ray analysis was separately pulverized, changes could have been introduced by either pulverizing the sample inadequately or pulverizing the sample too much. The powder photograph taken after four days has a grainy appearance to the lines which was due to inadequate pulverization of the sample (61). If the sample were pulverized too much, which is difficult to do, the lines would be broader and more diffuse.

Changes which occurred during the remaining four weeks were curious because one of the most intense lines in the x-ray photograph disappeared entirely, while other, less intense lines remained essentially unchanged. To find an explanation of what was happening during the "aging" process, the x-ray photograph of rhenium dioxide was compared to the photographs of the "aging" rhenium(V) chloride and intense lines of rhenium dioxide which might be appearing in the x-ray photographs of aging rhenium(V) chloride were sought. One of the lines in the powder pattern of rhenium dioxide, Table IX, page 40, at a d- spacing of 3.44 suggests that rhenium dioxide may be formed because of the appearance of a line at a d- spacing of 3.42 in the powder pattern of "aging" rhenium(V) chloride. Similarly the line at a d- spacing of 2.6 in the powder pattern of "aged" rhenium(V) chloride may be partially due to rhenium dioxide whose powder pattern has a line at a d- spacing of 2.56.

As the "aging" progressed, the powder photographs became more diffuse. This was due to a loss of crystallinity (61) which may have been caused by the appearance of several new species on the surface of rhenium(V) chloride. These new species would be present as very small, poorly formed crystals.

Hydrolysis of rhenium(V) chloride would be expected to form rhenium dioxide and perrhenate (62) at the surface. Such reactions would destroy the order of the microcrystals by imposing a second or third kind of order on the arrangement of rhenium(V) chloride. This

would effectively reduce the crystal size and result in broader, more diffuse lines, as observed.

Infrared Spectra

An infrared spectrum of the sample which was "aged" for six weeks was compared to spectra of rhenium dioxide, ammonium perrhenate and trioxochlororhenium(VII) as shown in Table X, page 41. This comparison showed evidence for the presence of some oxygen-containing species. It is reasonable to expect that oxo- species would be formed. The most likely reaction is the hydrolysis of rhenium(V) chloride which produces rhenium dioxide and perrhenic acid (6). Grove and Wilkinson (62) have suggested that the elusive oxotrichlororhenium(V) may be formed in hydrolysis reactions, but the only evidence for this proposal has been the observation of oxotrichlororhenium(V) with other ligands attached (triphenylphosphine, triphenylphosphine oxide). Frais et al.(63) reported the preparation of oxotrichlororhenium(V) but soon afterward described this conclusion as "arrant nonsense" (64). They found upon further analysis that it was /μ-oxo-bis{ oxotrichloro-(O-perrhenyl chloride)rhenium(VI)} , $ClReO_3 \cdot Re_2O_3Cl_6 \cdot O_3ReCl$.

Evidence for the presence of oxygen-containing species can be seen in the region between 1100 cm^{-1} and 700 cm^{-1}. Absorptions in this region, as indicated before, page 73, are indicative of the presence of rhenium-oxygen bonds. The spectrum shows absorptions at 1015 cm^{-1} and 915 cm^{-1} which are broad and of low intensity. These could be due to rhenium dioxide (915 cm^{-1}) and the perrhenate ion

which absorbs at about 900 cm^{-1}. The band at 1015 cm^{-1} is probably due to some other rhenium-oxygen species. These absorptions might arise from oxotetrachlororhenium(VI), trioxochlororhenium or the μ-oxo-bis{oxotrichloro(o-perrhenyl chloride)rhenium(VI)} $RClReO_3 \cdot ReO_3Cl_6 \cdot O_3ReCl$ (63), which have rhenium-oxygen absorption frequencies near the observed frequency. No conclusion can be made concerning the origin of this band. It could be due to the as yet unisolated oxotrichlororhenium(V), but this seems unlikely.

Because of the very poor quality of the spectrum obtained in the region between 500 cm^{-1} and 250 cm^{-1}, it was not possible to draw any conclusion concerning what species might be present.

On the basis of infrared spectroscopy substantive conclusions could not be drawn concerning the relative amounts of the components of "aged" rhenium(V) chloride. The problems which preclude even a semi-quantitative determination of the amounts include the concentration, path length, molar absorptivity, as well as instrument variables (65).

Elemental Analysis

Analysis made of the samples during the "aging" process are shown in Table XI, page 42. These show that the percentage of rhenium increases. The analysis at the end of six weeks (69.2% Re) fits with the theoretical rhenium content for trioxochlororhenium(VII), but "aged" rhenium(V) chloride cannot be this compound, because "aged" rhenium(V) chloride does not have a low enough melting point to be

trioxochlororhenium(VII). Furthermore, if it were trioxochlororhenium (VII) the x-ray powder photograph would not be as diffuse. It is more likely that "aged" rhenium(V) chloride is a mixture.

This mixture would need to consist of compounds with a high percentage of rhenium in order to explain the analysis results. It would also need to consist of oxygen-containing species, because analysis of the infrared spectrum suggested that these were present. It would also need to undergo the changes observed in the x-ray analysis which suggest some reaction. Since the sample was stored in the glove box, there was nitrogen as well as small amounts of water and oxygen present. There are no known reactions between rhenium(V) chloride and nitrogen used as an inert atmosphere. Rhenium(V) chloride is stable in the presence of dry oxygen (2). Therefore, the only reaction possible is with water. Table XXIII shows the theoretical rhenium content for various possible components of the mixture.

The mixture does not contain either of the lower chlorides, rhenium(III) chloride and rhenium(IV) chloride, because they are formed only upon heating rhenium(V) chloride to at least 250°C. This temperature does not occur in the glove box. Of the remaining possibilities, it is reasonable to expect that rhenium(V) chloride is still present. This is indicated by the x-ray data which after six weeks exhibits d- spacings which could arise from rhenium(V) chloride. Oxotetrachlororhenium(VI) is probably present because it was present in the original sample and because of the band in the infrared at 1015 cm^{-1}. The infrared band observed at 910 cm^{-1} does not distinguish

TABLE XXIII

RHENIUM CONTENT FOR SUGGESTED SPECIES PRESENT IN "AGED" RHENIUM(V) CHLORIDE

Compound	Percent Rhenium
ReO_2	85.3
$HReO_4$	74.1
ReO_3Cl	69.0
$ReCl_3$	63.6
$ReOCl_3$	60.3
$ReCl_4$	56.7
$ReOCl_4$	54.1
$ReCl_5$	51.2
H_2ReOCl_5	48.9

between rhenium dioxide and the perrhenate ion. Rhenium dioxide is suggested by one or two lines in the x-ray powder pattern. Analysis also suggests the formation of components with a high rhenium content such as rhenium dioxide and/or the perrhenate ion. Of the choices which remain the most likely constituent would be trioxochlororhenium (VII), which would satisfy the infrared band at 1015 cm^{-1} and the trend of the analysis toward higher rhenium content. The presence of oxotrichlororhenium(V) is questionable because of its apparent lack of stability as a separate species. It has been proposed as an intermediate in the reaction (62)

$$ReCl_5 + H_2O \rightleftharpoons [ReOCl_3] + 2HCl \rightleftharpoons H_2ReOCl_5$$

which occurs in acidic solution, but has not been isolated. Since the oxopentachlororhenate(V) species is produced in the same reaction as the postulated oxotrichlororhenium(V), it is also a possibility, but it seems unlikely because it has a low rhenium analysis and it is improbable that the acidity needed to produce that species would be present in the glove box.

The data are consistent with Rouschias' (2) observation that the "aged" material is a partially hydrolyzed sample of rhenium(V) chloride. It seems likely that the hydrolysis would continue until there would be no rhenium(V) chloride present, and only rhenium dioxide and the perrhenate ion would be left as products of the hydrolysis (5).

SOLVENT STUDIES WITH RHENIUM(V) CHLORIDE

The need to find a solvent was generated by a desire to study reactions of rhenium(V) chloride as well as its properties in solution. Properties such as the equivalence of the chlorines, the existence of a dimeric species in solution and the solution spectra were important before research into the formation of cluster compounds of rhenium(V) chloride could be undertaken.

Previous studies of rhenium(V) chloride with acetone have shown that it dissolves and, perhaps, reacts. Gehrke and Eastland (8) and Johnson et al.(28) have discussed the importance of acetone being dry and the effect of water on the products formed when triphenylphosphine is added to an acetone solution of rhenium(V) chloride. Johnson et al. (27) and Cotton et al.(29) have used acetone solutions of rhenium(V)

chloride to prepare pyridine complexes. Grove and Wilkinson (62) have discussed the hydrolysis of rhenium(V) chloride in wet acetone and have postulated oxotrichlororhenium(V) as an intermediate. Diethyl ether has been used as a solvent (66) for rhenium(V) chloride in attempts to prepare trimethylrhenium, but it is not clear if the ether was dry or if the reaction was carried out under anhydrous conditions. Acetic acid (67) with acetic anhydride added has been described as reacting in a nitrogen atmosphere with rhenium(V) chloride at reflux to produce trichlorodiacetatorhenium(V). Methylene chloride has been used as a solvent (28) in a reaction of rhenium(V) chloride and triphenylphosphine producing a product which was formulated as tetrachloro(triphenylphosphine)rhenium(IV). Later this formulation was shown to be incorrect. It should have been oxotrichlorobis(triphenylphosphine)rhenium(V) (8). It has been shown (30) that rhenium(V) chloride reacts with nitriles leading to products of the general formula $ReCl_4(RCN)_2$. Prior to the beginning of this work it was shown (31) that cyclic ethers produced compounds of the general formula $ReCl_4(L)_2$, (L=1,4-dioxane, tetrahydrofuran, and thiooxane) when rhenium (V) chloride was placed directly in the anhydrous ether.

The study which relates most directly to the present work was that of Smardzewski (20). This was important because he suggested that cyclohexane would be a useful solvent for rhenium(V) chloride. This was shown by the infrared spectrum of rhenium(V) chloride which was the same as the nujol spectrum of rhenium(V) chloride. Horner et al. (26) found that rhenium(V) chloride could be extracted from

hexachlororhenates with carbon tetrachloride. Furthermore, the rhenium (V) chloride could be recovered from the solution as rhenium(V) chloride.

The preceding summary of solvent interactions with rhenium(V) chloride points out the need to use anhydrous solvents in order to avoid hydrolysis reactions. It also points out the ease with which rhenium (V) chloride undergoes reaction.

Carbon Tetrachloride

Carbon tetrachloride was chosen as a solvent because of the work of Horner et al.(26) which was discussed earlier (page 88). It was also suggested by the work of Fairbrother et al.(46) where they used carbon tetrachloride in their solution studies on niobium(V) and tantalum(V) chlorides.

It has been indicated in Table XII, page 43 that only a small amount of rhenium(V) chloride dissolved in carbon tetrachloride, producing a green solution from which rhenium(V) chloride could not be recovered. An electronic spectrum of the solution showed a band at 420 nanometers which compares well with a band reported by Al-Mowali and Porte (68) for the electronic spectrum of oxotetrachlororhenium(VI). The electronic spectrum of oxotetrachlororhenium(V) exhibited bands at 781 nanometers and 571 nanometers which were assigned as $\underline{d} \leftarrow \underline{d}$ transitions. A band at 420 nanometers was assigned as a Re$\leftarrow$Cl charge transfer band. Presumably this was due to an allowed transition for which the observed band would be intense, with a molar absorptivity of around 10^4 (41). The fourth band observed in the electronic

spectrum of oxotetrachlororhenium(VI) was at 312 nanometers and was probably due to intraligand electron transfer. The band observed in the carbon tetrachloride solution of rhenium(V) chloride could be due to the charge transfer band of oxotetrachlororhenium(VI). Other bands were not observed because of the low concentration of the solution. Edwards and Ward (21) have described the diffuse reflectance spectrum of rhenium(V) chloride and found a band at 618 nanometers which they assigned to a $\underline{d} \leftarrow \underline{d}$ transition. A charge transfer band was found at 476 nanometers and intraligand transfer bands were observed at 260 nanometers and 232 nanometers. The absence of the band at 476 nanometers, or near that wavelength, in the carbon tetrachloride solution of rhenium(V) chloride suggests that either rhenium(V) chloride was not present in the solution or it was present at such a low concentration that the spectrum was not observed.

Removal of the solvent produced a dark gray solid. The x-ray powder photograph of this had few lines and those lines were broad and very diffuse. Again, as in the discussion of "aged" rhenium(V) chloride, this suggests that some material or materials are present which have very little crystallinity. This would most likely be caused by some type of reaction. Two reactions seem most likely. The first is a hydrolysis reaction involving water which was not totally removed from the solvent. Moisture may also have been introduced by a vacuum leak, though none was detected in these experiments. The second likely reaction is the formation of a complex with carbon tetrachloride which would again alter the crystallinity and perhaps cause the observed

changes in the x-ray powder pattern. A comparison of the x-ray powder patterns with powder patterns of rhenium(IV) chloride, rhenium(III) chloride, rhenium dioxide and oxotetrachlororhenium(VI) revealed no evidence for the presence of these species. This does not eliminate the possibility of the material recovered from the solution being a mixture of these compounds. The x-ray powder photograph has broad diffuse lines which, as discussed before, can be caused by crystals which are too small. It was expected that rhenium(IV) chloride might be formed, because it has been shown (32) that molybdenum(V) chloride is reduced to molybdenum(IV) chloride after lengthy contact with carbon tetrachloride. However, there was no evidence to indicate that rhenium (IV) chloride was present, which points out a difference between rhenium(V) chloride and molybdenum(V) chloride. The same observation of reduction by carbon tetrachloride may have also led to the formation of rhenium(III) chloride in the solution. However, none was found in the material recovered from the solution. Even if rhenium(III) chloride had been found, it would probably require reduction by something other than carbon tetrachloride. Rhenium dioxide would have been formed as a result of the hydrolysis (6) of rhenium(V) chloride which would result from the presence of water in the carbon tetrachloride or moisture entering the system as a result of a leak in the system. The presence of oxotetrachlororhenium(VI) was expected because it was present in the original sample.

It has been suggested (46) that niobium(V) and tantalum(V) chloride dissolve in carbon tetrachloride with the formation of a complex.

The possibility that the material which was recovered from the carbon tetrachloride solution was a complex of carbon tetrachloride was considered. Such a complex should show strong infrared absorption somewhat below 750 cm^{-1}-800 cm^{-1}, which is where carbon-chlorine absorptions occur in carbon tetrachloride (69). None are observed in the infrared spectrum. This suggests either that no complex is formed between rhenium(V) chloride and carbon tetrachloride or that it is unstable and not present in the solid.

Horner et al.(26) found that rhenium(V) chloride could be recovered from a red solution which was formed by extracting what was thought to be rhenium(V) chloride from the reaction for the formation of hexachlororhenates,

$$4MReO_4 + 16CCl_4 \longrightarrow 2M_2ReCl_6 + 2Re_2Cl_5 + 5Cl_2 + 16COCl_2.$$

(M = Li, Na, K, Cs, Cu(I), Ag, Tl(I), Ba and Cu(II))

Since the reaction was carried out at elevated temperatures it was possible that monomeric rhenium(V) chloride was formed, while at room temperature only the dimeric form was present. Perhaps if the temperature of the solution were raised, it would be possible to dissolve rhenium(V) chloride in carbon tetrachloride by producing the monomeric species.

When the material which was recovered from the solution was heated to 350°C, in an attempt to determine its melting point, it was changed into rhenium(III) chloride, as was shown by infrared spectroscopy and x-ray powder photography. It was also shown by the reaction of

triphenylphosphine in acetone, which produced trichloro(triphenylphosphine)rhenium(III), $ReCl_3\left[(C_6H_5)_3P\right]$. Cotton et al. (70) and Colton et al.(71) have shown that this species is produced only from rhenium (III) chloride. Rhenium(III) chloride was produced in the melting point tube without apparent melting. It is known (22) that heating liquid rhenium(V) chloride in a nitrogen atmosphere produces rhenium(III) chloride which suggests that rhenium(V) chloride was not present in the melting point tube, since no melting was observed. Yet, rhenium(III) chloride was formed, which suggests that perhaps there was some rhenium (V) chloride present. The presence of the rhenium(V) chloride could have been undetected because of a change in form or a reaction with carbon tetrachloride of the type suggested by Frais et al. (63). They found that rhenium trioxide and rhenium(V) chloride would form an oxo-species which dissolves in carbon tetrachloride and readily decomposes to rhenium(III) chloride. However, formation of rhenium trioxide is difficult to explain under the circumstances which exist in this instance because of the difficulty in preparing it (5).

The carbon tetrachloride which was removed from the solution revealed, when examined by chromatographic separation, no impurities at the level of detection (10^{-11} gm.) of the mass spectrometer used. This indicates that any reactions which did take place did not alter the integrity of the carbon tetrachloride.

Reaction of Triphenylphosphine with Oxotetrachlororhenium(VI)

Eastland (53) briefly examined the reaction of rhenium(V) chloride in carbon tetrachloride with triphenylphosphine. A tentative suggestion was made that from the complexity of the infrared spectrum, the product probably had the solvent incorporated within it in some way. In this work, a second examination of this reaction was made. As a result of this examination it was possible to determine in part what dissolved in carbon tetrachloride and to determine what complex was formed with triphenylphosphine in carbon tetrachloride solution.

When triphenylphosphine was added to the filtered solution of rhenium(V) chloride in carbon tetrachloride, an immediate precipitate was formed. Elemental analysis was consistent with the empirical formula, $ReCl_4C_{36}H_{30}P_2O$. The infrared spectrum revealed the presence of coordinated triphenylphosphine oxide and triphenylphosphine. Absorption bands at 1124 cm^{-1} and 1142 cm^{-1} were probably due to the P-sensitive q-mode and the P=O stretching frequency of coordinated triphenylphosphine oxide (72)(73)(74). In the same general region of the spectrum, at 1091 cm^{-1}, was a band which could be assigned to the P-sensitive q-mode of coordinated triphenylphosphine (72)(73)(74). In a similar compound, oxotrichloro(triphenylphosphinetriphenylphosphine oxide)rhenium(V), $ReOCl_3\left[(C_6H_5)_3P\right]\left[(C_6H_5)PO\right]$ (47), the infrared spectrum exhibited bands which were attributed to coordinated triphenylphosphine at 1090 cm^{-1} and coordinated triphenylphosphine oxide at 1110 cm^{-1} and 1140 cm^{-1}. This is in good agreement with the observed spectrum for tetrachloro(triphenylphosphinetriphenylphosphine

oxide)rhenium(IV), $ReCl_4[(C_6H_5)_3P][(C_6H_5)_3PO]$. There was also a set of bands at a lower frequency which were related to the phosphine-phosphine oxide moieties. These bands are: 1) 690 cm^{-1}, probably due to carbon-carbon stretching frequencies of both triphenylphosphine and triphenylphosphine oxide, 2) a shoulder at 702 cm^{-1} which can be assigned to the x-sensitive mode of coordinated triphenylphosphine, and 3) 726 cm^{-1}, probably due to the x-sensitive mode of coordinated triphenylphosphine oxide. In addition, there is a pair of intense bands at 525 cm^{-1} and 532 cm^{-1} which are probably due to an x-sensitive mode of coordinated triphenylphosphine and coordinated triphenylphosphine oxide, respectively. The rhenium-chlorine stretching frequency is found at 316 cm^{-1}. This is in the same region as other rhenium(IV) tetrachloro- complexes. These are tabulated in Table XXIV, page 96. The color of tetrachloro(triphenylphosphinetriphenylphosphine oxide) rhenium(IV), $ReCl_4[(C_6H_5)_3P][(C_6H_5)_3PO]$, yellow-green, is consistent with the formulation as indicated in Table XXIV, page 96, where it is shown that other tetrachlororhenium(IV) complexes have similar colors, particularly those which have an oxygen coordinated to the rhenium.

A question which is raised by this formulation is: Where does the oxygen for the triphenylphosphine oxide ligand come from? Carbon tetrachloride was carefully purified and triphenylphosphine was recrystallized. It would seem that the oxygen was from another source. Dissolved oxygen in the solvent was a possibility. However, the use

TABLE XXIV

RHENIUM-CHLORINE INFRARED ABSORPTION FREQUENCY AND COLOR OF SOME COMPLEXES OF THE GENERAL FORM $ReCl_4L_2$

Complex	Re Cl (cm^{-1})	Color	Reference
$ReCl_4[(C_6H_5)_3P]_2$	321	red-brown	(75)
$ReCl_4[(C_6H_5)_3PO]_2$	308	green	(47)
$ReCl_4(C_4H_8O_2)_2$	335	green	(31)
$ReCl_4(C_4H_8O)_2$	335	green-yellow	(31)

of degassed carbon tetrachloride did not affect the formation of tetrachloro(triphenylphosphinetriphenylphosphine oxide)rhenium(IV), $ReCl_4[(C_6H_5)_3P][(C_6H_5)_3PO]$.

In an earlier part of this discussion it was pointed out that there is a band at 1036 cm^{-1} in the infrared spectrum of rhenium(V) chloride which could be caused by the presence of some rhenium-oxygen species, possibly oxotetrachlororhenium(VI). If this was the impurity and if it dissolves in carbon tetrachloride, then it could very likely be the species which reacts with triphenylphosphine. This was tested by dissolving some oxotetrachlororhenium(VI) in carbon tetrachloride. It was found that 2.02 grams of oxotetrachlororhenium(VI) dissolved in about fifty milliliters of carbon tetrachloride giving a green solution, just as did carbon tetrachloride and rhenium(V) chloride, and no evidence of a residue. Addition of triphenylphosphine to the solution

resulted in formation of a green precipitate which, when isolated, gave the same infrared spectrum as the product of the reaction between the material which was present in rhenium(V) chloride and dissolved in carbon tetrachloride and reacted with triphenylphosphine. The yield was 83%, based on 2.02 grams oxotetrachlororhenium(VI).

A solution of oxotetrachlororhenium(VI) chloride in carbon tetrachloride was prepared under high vacuum, in the same apparatus used in other solution studies (Figure 5, page 33). It was found that complete dissolution occurred within a very short time. Oxotetrachlororhenium (VI) was recovered from the solution unchanged, as indicated by its infrared spectrum and its electronic spectrum which were identical to spectra taken before oxotetrachlororhenium(VI) was dissolved. Because of the low melting point of oxotetrachlororhenium(VI) (ca. 30°C) it was found that an x-ray capillary tube could not be filled to obtain an x-ray powder photograph. A melting point determination was made with most of the material melting, as expected, below 30°C. There was however a small portion of the material in the tube which would not melt even at 350°C. Because of the presence of the low melting species, no attempt was made to determine if rhenium(III) chloride was present.

These results do suggest that there must have been some other species, in addition to oxotetrachlororhenium(VI), present in the material which was recovered from the carbon tetrachloride to account for its behavior.

The reaction between triphenylphosphine and oxotetrachlororhenium(VI) could occur by direct reaction between triphenylphosphine

and oxygen on the oxotetrachlororhenium(VI). The crystal structure of oxotetrachlororhenium(VI) (76) suggests a very weak long range bridge between rhenium and chlorine trans to the oxygen. This bridge is probably not present in the solution (77) and would readily accept a triphenylphosphine trans to the oxygen.

Further support for this compound being formed from oxotetrachlororhenium(VI) rather than from rhenium(V) chloride is to be found in Table XXV. In this table the amount of oxotetrachlororhenium(VI)

TABLE XXV

COMPARISON OF AMOUNT OF $ReOCl_4$ REQUIRED TO FORM $ReCl_4\left[(C_6H_5)_3P\right]\left[(C_6H_5)_3PO\right]$

$ReCl_4\left[(C_6H_5)_3P\right]\left[(C_6H_5)_3PO\right]$ Formed	$ReOCl_4$ Required	$ReOCl_4$ Dissolved
0.10	0.04	0.06
0.17	0.07	0.05
0.12	0.05	0.05
0.17	0.07	0.08

dissolved was determined by the difference between the mass of rhenium (V) chloride placed in the reaction tube and the mass of rhenium(V) chloride recovered from the reaction tube and the filter tube after the solution had been filtered. The mass of oxotetrachlororhenium(VI) required was calculated on the basis of the amount of tetrachloro(triphenylphosphinetriphenylphosphine oxide)rhenium(IV), $ReCl_4\left[(C_6H_5)_3P\right]\left[(C_6H_5)_3PO\right]$, produced. The correlation was good.

This amount of material dissolved is also in agreement with the amount which dissolved and was recovered from carbon tetrachloride in the vacuum line experiments. In those experiments it was found that between 0.05 gram and 0.09 gram dissolved.

Though the evidence is less conclusive than that presented for the material which dissolves in carbon tetrachloride, it seems likely that what dissolves in chloroform and cyclohexane is oxotetrachlororhenium(VI) and not rhenium(V) chloride. The evidence which suggests this is that nearly the same amount of material was dissolved in chloroform and cyclohexane as in the carbon tetrachloride. The solution produced was green in color and, in the case of chloroform, the material recovered from the solution behaved in the same way as that which was recovered from the carbon tetrachloride solution. An experiment which would test this hypothesis would involve adding triphenylphosphine to the solution after it had been filtered. It would be expected that tetrachloro(triphenylphosphinetriphenylphosphine oxide)rhenium(IV), $ReCl_4\left[(C_6H_5)_3P\right]\left[(C_6H_5)_3PO\right]$, would be produced as in the carbon tetrachloride solution.

In conclusion, tetrachloro(triphenylphosphinetriphenylphosphine oxide)rhenium(IV), $ReCl_4\left[(C_6H_5)_3P\right]\left[(C_6H_5)_3PO\right]$, is formed by reaction of a carbon tetrachloride solution of oxotetrachlororhenium(VI) with triphenylphosphine. Samples of rhenium(V) chloride used in this research have been contaminated with oxotetrachlororhenium(VI) which is probably present in the sample from the time it was prepared. Extensive attempts to purify rhenium(V) chloride have been unsuccessful

in removing the oxotetrachlororhenium(VI) impurity. As Guest and Lock (58) found, oxygen is very difficult to remove entirely from the system used to prepare rhenium(V) chloride.

Further, it is concluded that infrared spectra which have been reported (20)(21) are spectra of rhenium(V) chloride with some contamination by oxotetrachlororhenium(VI). The correlation between d- spacings found from the x-ray powder photograph of rhenium(V) chloride used in this research and the d- spacings calculated from the data produced by the crystal structure determination (11) of rhenium(V) chloride suggests that the rhenium(V) chloride used in this research has the same crystal structure as that on which the determination was made. This, together with the absence of rhenium-chlorine infrared absorption bands between 500 cm^{-1} and 250 cm^{-1} which could be assigned to oxotetrachlororhenium(VI), leads to the conclusion that the rhenium(V) chloride used in this work was purer than that used by others (20)(21) to obtain infrared data. Therefore the infrared spectrum obtained in this work is more representative of rhenium(V) chloride than those reported by Smardzewski (20) and Edwards and Ward (21).

The conclusion that oxotetrachlororhenium(VI) is the material which dissolves also suggests the reason why more material does not dissolve. If any rhenium(V) chloride dissolves, it is a very small amount. If all of the oxotetrachlororhenium(VI) is removed from rhenium(V) chloride and rhenium(V) chloride does not dissolve, then the amount of oxotetrachlororhenium(VI) limits the total amount of material which dissolves. This leaves unexplained the formation of rhenium(III) chloride when the

material recovered from the solution was heated. It cannot be accounted for on the basis of heating oxotetrachlororhenium(VI), since this liquifies at about 30°C. It was also shown that the material recovered from the carbon tetrachloride was probably not oxotetrachlororhenium(VI) because it did not melt at about 30°C. This suggests that some rhenium(V) chloride may have dissolved and was present in some form which has a higher melting point. An alternative explanation was suggested by Frais et al.(63) and Calvo et al.(64)—the existence of μ-oxo-bis {oxotrichloro(O-perrhenyl chloride)rhenium(VI)}, $ReClO_3 \cdot Re_2O_3Cl_6 \cdot O_3ClRe$, which they found behaves in an apparently similar way to the material which was recovered from the carbon tetrachloride-rhenium(V) chloride solution. This material, when heated, changes to rhenium(III) chloride.

Chloroform

Chloroform, when used as a potential solvent, produced nearly the same results as found for carbon tetrachloride. The only different observation made was in the examination of the solvent, which indicated the presence of tetrachloroethylene. The formation of this species cannot be definitely tied to the presence of rhenium(V) chloride without further work because of the possibility of a photochemical formation of tetrachloroethylene.

The interaction of chloroform with rhenium(V) chloride dissolved only 0.03 gram of material. The material which dissolved was not recovered from the solution as rhenium(V) chloride. In the same way

as with the carbon tetrachloride interaction, the material which was recovered from the solution, when heated in a sealed melting point capillary, did not melt, but formed rhenium(III) chloride. Identification of rhenium(III) chloride was described in the discussion of the carbon tetrachloride interaction.

Cyclohexane

Cyclohexane was selected as a potential solvent because Smardzewski (20) was able to obtain infrared spectra of rhenium(V) chloride in cyclohexane. It was also selected because it had been used by Fairbrother et al. (51) as a solvent for tantalum(V) chloride. It was found, in this work, that only a very small amount (0.03 gram) of rhenium(V) chloride dissolved. An infrared spectrum of the cyclohexane solution was obtained and only an absorption band at 302 cm^{-1} could be distinguished from the solvent bands. Perhaps other absorptions are present but obscured by the bands of the solvent. A band does appear at 301 cm^{-1} in the nujol spectrum of rhenium(V) chloride, but it is not a strong absorption, so the spectrum in cyclohexane is not the spectrum of rhenium(V) chloride because it would only be the bands associated with strong absorptions which would appear in a dilute solution. In the electronic spectrum, an absorption band was observed at 408 nanometers. An extremely weak band was also noted at 625 nanometers. It is possible that the band at 625 nanometers was due to rhenium(V) chloride. The diffuse reflectance spectrum of rhenium(V) chloride was reported (21) as having a band at 618

nanometers. The diffuse reflectance spectrum of rhenium(V) chloride shows a band at 476 nanometers as the closest band to the observed 408 nanometer band. However, the electronic spectrum of oxotetrachlororhenium(VI) (68) exhibits a band at 420 nanometers. This 420-nanometer band has been assigned as a metal ion-chloride ion charge transfer band (68) and as such should be quite intense (78), as indeed was observed. This suggests that perhaps the species present in the solution is oxotetrachlororhenium(VI).

The observation of an absorption band at 625 nanometers which might be due to rhenium(V) chloride is difficult to explain. The band which was reported at 618 nanometers was assigned as a $\underline{d} \leftarrow \underline{d}$ transition (21). Such transitions normally are of low intensity (41) while charge transfer bands, such as the one at 476 nanometers (21) are of high intensity. Yet, there was no evidence for a band at or near 476 nanometers in the spectrum of rhenium(V) chloride in cyclohexane. This suggests that the band observed at 625 nanometers was not due to rhenium(V) chloride but to some other species in the solution. These observations, together with the infrared spectrum of the cyclohexane solution further suggest that the spectrum obtained by Smardzewski (20) was the spectrum of some other material than rhenium(V) chloride.

When the solvent was removed from the solution only an oily material was left in the filtrate tube. Because of the small amount present and the fact that it was coating the walls, no further work was done.

Summary of Solvent Studies

It was concluded that carbon tetrachloride, chloroform and cyclohexane would not be useful as solvents for studying the solution chemistry of rhenium(V) chloride. There are two reasons for this conclusion: 1) The material which dissolves either did not remain rhenium (V) chloride or it was not rhenium(V) chloride when dissolution occurred. 2) There was only a very small amount of material which did dissolve.

There was no evidence to indicate that an adduct of carbon tetrachloride or chloroform had formed. If an adduct had formed the infrared spectrum would have revealed carbon-chlorine absorption bands near 750 cm^{-1} (68). Absorptions were not observed in this region.

The results which have been observed in this work are not consistent with those found by other workers. Horner et al.(26) were able to extract rhenium(V) chloride from other reaction products with carbon tetrachloride while only a very limited amount of rhenium(V) chloride was found to dissolve in this research. The basic difference between the two systems was the way in which rhenium(V) chloride was formed. The possibility exists that they could have a different form of rhenium(V) chloride which would be more soluble in carbon tetrachloride than what has been found in this work. This possibility was also suggested by Fairbrother et al. (46) in their solvent studies. They found niobium(V) and tantalum(V) chlorides remain dimeric in carbon tetrachloride but the possibility of a monomeric species was discussed. It has been suggested (46) that a weak complex between solvent and solute was formed with niobium(V) and tantalum(V) chlorides,

but no evidence was found for this in the case of rhenium(V) chloride. Molybdenum(V) chloride has been found (32) to undergo reduction to molybdenum(IV) chloride but no evidence was found which would suggest that this occurred with rhenium(V) chloride. Rhenium(V) chloride does not behave in a manner similar to these other pentachlorides and no particular reason is apparent.

Rhenium(V) chloride in this work does not dissolve in cyclohexane as was found by Smardzewski (20). It seems that what Smardzewski was examining was oxotetrachlororhenium(VI) in the solution rather than rhenium(V) chloride. This is suggested by the similarity between the infrared spectrum which he obtained in nujol and the infrared spectrum of oxotetrachlororhenium(VI) which was obtained in this work and the fact that his nujol spectrum was very similar to the spectrum which he obtained in cyclohexane solution. Fairbrother et al.(46) have found that niobium(V) and tantalum(V) chloride dissolve in cyclohexane with perhaps some weak solvent interaction. This again points out the difference between rhenium(V) chloride and the pentachlorides of niobium and tantalum.

ADDUCT FORMATION STUDIES

As a result of the above conclusions it was decided to consider solvents which might form simple adducts. There are no reports of the formation of simple adducts of rhenium(V) chloride. Since there are reports of simple adducts being formed between niobium(V) and tantalum (V) chlorides and 1,4-dioxane (44) and diethyl ether (45) as well

as an adduct between 1,4-dioxane and molybdenum(V) chloride (32), these two solvents were chosen to investigate the formation of adducts of rhenium(V) chloride.

1,4-dioxane

Allen et al. (31) had examined the reaction with 1,4-dioxane and rhenium(V) chloride in sealed tubes. After a reaction time of three days, they found not a simple adduct or an oxygen-containing species, but an addition product, tetrachlorobis(1,4-dioxane)rhenium(IV), $ReCl_4(C_4H_8O_2)_2$. The idea that perhaps a shorter reaction time would serve to form an adduct was suggested in the work of Keppert and Mandyczewski (32) in which they found that molybdenum(V) chloride formed an adduct at short reaction times, while oxygen abstraction occurred at longer reaction times. The 1,4-dioxane was left in contact with rhenium(V) chloride for one hour and removed, leaving a pale green solid. Comparison of the infrared spectrum and the electronic spectrum obtained with those reported by Allen et al. (31) showed that after only one hour of reaction, tetrachlorobis(1,4-dioxane)rhenium(IV), $ReCl_4(C_4H_8O_2)_2$, was formed.

Examination of the 1,4-dioxane removed from the solution revealed no detectable species besides 1,4-dioxane. In the work with molybdenum (V) chloride (32) it was found that 2,2'-dichlorodiethylether was produced in the reaction.

Thus, the present work is in agreement with the findings of Allen et al. (31). It also points out the difference between rhenium(V) chloride and pentachlorides of molybdenum, tantalum and niobium.

Diethyl Ether

When diethyl ether reacted with niobium(V) and tantalum(V) chloride, the adducts, pentachloro(diethyl ether)niobium(V), $NbCl_5 \cdot CH_3CH_2OCH_2CH_3$, and pentachloro(diethyl ether)tantalum(V), $TaCl_5 \cdot CH_3CH_2OCH_2CH_3$, were formed. When heated, these adducts produced oxotrichloroniobium(V) and oxotrichlorotantalum(V) (45), respectively. This suggests that perhaps if diethyl ether would form an adduct with rhenium(V) chloride, it might be decomposed to produce the as yet unisolated oxotrichlororhenium(V) species rather than simply giving up the diethyl ether to regenerate rhenium(V) chloride. Diethyl ether was also suggested as a solvent for rhenium(V) chloride by some early work (66) in which the formation of trimethylrhenium was attempted. In that study a green solution was observed but no indication was made concerning the species present in the reaction.

When diethyl ether and rhenium(V) chloride were mixed in the vacuum filtration apparatus, a brownish-red solution was observed, leaving a brown residue when the solvent was removed. Recrystallization of the moisture-sensitive material was unsuccessful, perhaps as a result of moisture in the solvents, even though they were dried before use. An infrared spectrum of the brown residue suggests that coordination of diethyl ether has occurred. This is suggested by the shift of the C-O-C absorption frequency from its uncoordinated 1120 cm^{-1} (69)(78) to the coordinated frequency at 1015 cm^{-1}. A shift of 105 cm^{-1} is somewhat larger than a similar shift ($\Delta\nu$ = 73 cm^{-1}) observed by Allen et al. (31) for tetrahydrofuran when it was

coordinated to rhenium in tetrachlorobis(tetrahydrofuran)rhenium(IV), $ReCl_4(C_4H_8O)_2$. They found that it shifted frequency from 1071 cm^{-1} for the uncoordinated C-O-C frequency of tetrahydrofuran to 998 cm^{-1} for the coordinated tetrahydrofuran. This is a reasonable comparison based on a study by Bellamy (69) in which it was found that chain size had little effect on the location of the ν C-O-C frequency. Similarly, as the size of the ring of the cyclic ether increased from a three-member ring to a five-member ring, the ring strain was reduced and the ν C-O-C frequency was nearly that of open-chain compounds. Then it is reasonable to expect that coordination by an ether oxygen to a metal in the same environment should produce about the same shift in the ν C-O-C frequency.

A strong absorption band at 321 cm^{-1} is indicative of rhenium-chlorine bonds (31)(59). Furthermore, it is in the same region of the spectrum as are rhenium-chlorine absorption for complexes which are known to have a formulation of $ReCl_4L_2$. Table XXIV, page 96, contains a tabulation of known rhenium-chlorine frequencies for $ReCl_4L_2$ complexes. The brown color is also consistent with the formulation tetrachlorobis(diethyl ether)rhenium(IV), $ReCl_4\left[(C_2H_5)_2O\right]_2$, as shown in Table XXIV, page 96.

By analogy with the reaction of 1,4-dioxane with rhenium(V) chloride, the product of the reaction of diethyl ether with rhenium(V) chloride could be formulated as tetrachlorobis(diethyl ether)-rhenium(IV), $ReCl_4\left[(C_2H_5)_2O\right]_2$. This formulation can only be a very

tentative one and must await successful purification and elemental analysis to make a more positive identification.

When the solvent was removed from the solution it was examined by gas chromatographic analysis and peaks were identified by mass spectroscopy. There was observed in this analysis a peak which was due to a monochlorinated ether. Positive identification could not be made because no monochlorinated ethers were available to enable a comparison to be made. The observation of this monochlorinated ether lends further support to the proposed formulation for the brown material which was produced in this reaction, because the chlorine for the monochloroether would have come from rhenium(V) chloride in the reaction

$$ReCl_5 + 2CH_3CH_2\overset{O}{\diagup\diagdown}CH_2CH_3 \longrightarrow ReCl_4(CH_3CH_2OCH_2CH_3)_2 + 2Cl^-.$$

The chloride ions could then react with diethyl ether to form the monochlorinated ether.

Acetone

The choice of acetone as a solvent was made primarily to obtain direct evidence for the formation of the condensed acetone compound, 4-methyl-3-pentene-2-one, $\overset{CH_3}{\underset{CH_3}{C}} = CH-\overset{O}{\overset{\|}{C}}-CH_3$, which was postulated by Gehrke and Eastland (8) as having been formed in the reaction between rhenium(V) chloride and triphenylphosphine in acetone.

When acetone and rhenium(V) chloride were mixed, all of the rhenium(V) chloride dissolved, as expected. But what was not expected was the formation of a brown solution, because other reactions in

which acetone was used as a solvent produced a green solution. A possible explanation for this was found as the solvent was removed. This procedure took place very slowly when it was noticed that the pressure in the system was about 20 torr instead of 10^{-5} torr. This indicated that a leak had developed and might account for the brown color. Eventually, the solvent was removed, leaving an oily material deposited in the filtrate tube. A formulation of this material was not possible because of the intractable nature of the material.

A second difficulty with this experiment was found when the acetone which was used in the experiment was analyzed by gas chromatography. This analysis was made on a sample which had been purified but <u>did not contact</u> rhenium(V) chloride. Five separate species were found to be present in the acetone which had been purified. The source and identity of these species was sought but was not found. A gas chromatographic analysis of the acetone <u>prior</u> to purification also showed what appeared to be the same impurities. They were neither introduced nor removed by the purification process. When 4-methyl-3-pentene-2-one, $\begin{matrix} CH_3 \\ | \\ C \\ | \\ CH_3 \end{matrix} = CH-\overset{\overset{O}{\|}}{C}-CH_3$, was added to the <u>purified</u> acetone it produced a separate, distinct peak in the gas chromatographic separation. Therefore, it was still possible to determine if this species was formed by the interaction of rhenium(V) chloride with the acetone.

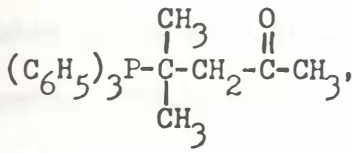
Gas chromatographic analysis of the solvent <u>after</u> it was removed from rhenium(V) chloride showed that no 4-methyl-3-pentene-2-one,

$\begin{matrix} CH_3 \\ | \\ C = CH \\ | \\ CH_3 \end{matrix}$ $\begin{matrix} O \\ \| \\ -C-CH_3 \end{matrix}$, had been produced in amounts great enough to be detected by gas chromatographic analysis.

Summary of Adduct Preparation Experiments

Simple adducts of rhenium(V) chloride were not prepared using 1,4-dioxane, diethyl ether and acetone. This work has confirmed the findings of Allen et al.(31) in the formation of tetrachlorobis(1,4-dioxane)rhenium(IV), $ReCl_4(C_4H_8O_2)_2$. Again, as has been pointed out in the earlier summary of solvent interactions, rhenium(V) chloride behaves in a different way than do other metal pentachlorides. Rhenium (V) chloride neither abstracts oxygen from 1,4-dioxane, as was found to be the case with molybdenum(V) chloride (32), nor does it form a simple adduct as do niobium(V) and tantalum(V) chloride with 1,4-dioxane (44). An interaction between rhenium(V) chloride and diethyl ether suggests the formation of tetrachlorobis(diethyl ether)rhenium(IV), $ReCl_4\left[(CH_3CH_2)_2O\right]_2$, which again is in contrast to the behavior of niobium(V) and tantalum(V) chlorides (45). No conclusion about the rhenium species which formed was possible in the interaction between rhenium(V) chloride because of the intractable nature of the material. Analysis of the solvent which was removed from the solution did not reveal the presence of the expected 4-methyl-3-pentene-2-one, $\begin{matrix} CH_3 \\ | \\ C = CH \\ | \\ CH_3 \end{matrix}$ $\begin{matrix} O \\ \| \\ -C-CH_3 \end{matrix}$, which Gehrke and Eastland (8) had postulated in their study. It is possible that leaks in the system prevented its

formation. It is also possible that triphenylphosphine, which was present in their system but absent in the present work, is necessary for the cation, 1,1-dimethyl-3-oxobutyltriphenylphosphonium,



, to form.

EVALUATION OF THE APPARATUS USED

It was pointed out in the experimental section that some problems arose with the vacuum filtration apparatus (Figure 5, page 33). One problem was the inconsistency of mass measurements. It will be recalled from the discussion of the experimental procedure (page 96) involved with the vacuum line solution experiments, that mass measurements involved three pieces of equipment plus assorted caps, rubber bands (used to hold the pieces together), stopcocks, grease and a stirring bar. To show the difficulty involved, consider the measurement of the mass of rhenium(V) chloride used. This was to be placed in the mixing tube along with a stirring bar. The mixing tube, with a greased joint, a glass cap, the stirring bar and a rubber band were assembled and the mass of the assemblage was determined. Following the mass determination, the assemblage was transferred to the glove box where it was disassembled and a sample of rhenium(V) chloride was placed into the tube. The parts were reassembled and removed from the glove box and the mass was determined again. The mixing tube was again returned to the glove box, its cap was removed, and the entire apparatus was assembled. The mass of each part of the apparatus was

determined before placing in the glove box. This meant that a cap for each of four joints as well as some of the rubber bands had to be left in the glove box while the experiment was conducted. Care was taken to be able to match caps and joints by etched identification marks. The rubber bands were marked so that the same ones could be used on the same part of the apparatus.

After an experimental trial, the solvent was removed and the entire apparatus was returned to the glove box where it was disassembled and the proper cap replaced on the proper joint, held in place with the correct rubber band. Then each piece was removed from the glove box and its mass was determined.

It is very possible that mass errors could result in any of several ways. The caps and/or rubber bands could be mixed up. There might have been a net transfer of grease from one piece to another. The solvent might have been incompletely removed. With all of the steps involved and the separate mass determinations made, there may have been an error in adjusting and/or reading the balance.

Some of these are less likely than others. Since the caps and rubber bands were identified and this source of error was recognized, extra care was exercised to be sure they were not mixed up. To assess the role of possible transfer of grease, a test was run in which the entire procedure was followed, with a resulting loss of less than 0.01 gram in the mass of the tubes; therefore, the transfer of grease is an unlikely cause for the problem observed.

Of the two sources of error which remain, there is little evidence which would suggest that one or the other would be primarily responsible. With dense solvents such as carbon tetrachloride and chloroform, failure to remove a fraction of a milliliter of the solvent could result in a sizeable relative mass increase. Errors in adjusting or reading the balance are difficult to analyze, but it is a possible source of error.

A second problem which dealt with the vacuum filtration apparatus was precipitated by a concern for contamination with grease. In an effort to avoid this problem, an apparatus similar to that shown in Figure 5, page 33, was constructed using o-ring joints instead of standard taper ground joints, and Teflon needle valves instead of stopcocks. Care was taken to choose an o-ring material which would not interact with the solvent. The choice of fluorocarbon rubber (Viton-A) was made for use with hydrocarbons and chlorinated hydrocarbons (57), while ethylene propylene rubber was chosen to use with ketones, ethers and other polar organic compounds (57). However, this apparatus developed a persistent leak which limited its effective use. The leak could not be isolated but was suspected of being caused by a minute imperfection in the glass of one of the o-ring joints.

A third problem which arose with the vacuum filtration apparatus was a more general problem which is always encountered in research involving a vacuum system—leakage. After a series of trials the vacuum system was disassembled for cleaning and renewing of the stopcock grease and o-rings at the various joints in the system. Upon reassembling the system, evacuating it, heating the glass, working in

the stopcocks and adjusting the o-rings, a leak remained which could not be located. Work on solution studies with the vacuum system was discontinued because of vacuum leakage and the low solubility of rhenium(V) chloride in carbon tetrachloride, chloroform and cyclohexane. Work was discontinued on adduct studies because of the intractability of the products.

ACETIC ACID AND RHENIUM(V) CHLORIDE

Taha and Wilkinson (78) have reported the reaction of rhenium(V) chloride with acetic acid which contained acetic anhydride. They found that this reaction produced a black solid, trichlorodiacetatorhenium(V), $[ReCl_3(CH_3COO)_2]_n$, and a black solution. This reaction was of interest because it had been noted that when acetic acid-acetic anhydride was added to rhenium(IV) chloride a pale green solution was formed (79). A relatively simple qualitative test for the presence of rhenium(IV) chloride would then be the addition of acetic acid-acetic anhydride to a suspected sample of rhenium(IV) chloride. The presence of a pale green color would confirm the presence of rhenium(IV) chloride, while a black color would suggest the presence of rhenium(V) chloride. Unfortunately, it was observed (79) that when rhenium(V) chloride was added to acetic acid-acetic anhydride but not refluxed, a turquoise color was produced.

This work confirms that a black solid is produced upon refluxing acetic acid-acetic anhydride with rhenium(V) chloride. However, the product obtained in this work was definitely not trichlorodiacetatorhenium(V), $[ReCl_3(CH_3COO)_2]_n$. This is shown by the very high rhenium

analysis (64.6%) and the very low chlorine analysis (1.6%). Furthermore, infrared spectroscopy provides no evidence for absorptions which would be due to an acetate group. A strong absorption would be expected near 1600 cm^{-1} and moderate absorption near 1400 cm^{-1} (78), but none were observed. The spectrum contains no band between 500 cm^{-1} and 250 cm^{-1} which is intense enough to be considered a rhenium-chlorine absorption. There is, however, a strong, broad band with a maximum at 910 cm^{-1}. This band suggests the presence of the perrhenate ion which absorbs at 910 cm^{-1}, Figure 10, page 159, and/or rhenium dioxide which has an infrared absorption at 910 cm^{-1}, Figure 19, page 162. A part of the sample dissolved in water. The water portion was decanted and tetraphenyl arsonium ion was added, producing a precipitate indicating that perrhenate was either present in the sample or was produced when water was added. The material which did not dissolve in water was shown to have an infrared spectrum like that of rhenium dioxide, with an absorption band at 910 cm^{-1}.

When all operations were carried out under nitrogen, the results of the reaction were the same. A nujol mull prepared in the glove box of a sample which was kept under nitrogen was the same as the spectra obtained of nujol mulls prepared on the bench top.

In conclusion, the reaction between rhenium(V) chloride and acetic acid-acetic anhydride did not form trichlorodiacetatorhenium(III), $[ReCl_3(CH_3COO)_2]_n$, in this work. Precautions were taken to maintain an anhydrous condition throughout. Even so, the possibility that hydrolysis had taken place must be considered because of the evidence

which suggests that rhenium dioxide and/or the perrhenate ion were produced. But hydrolysis requires the presence of water which had been guarded against by the use of acetic anhydride. It was observed that as long as the solution was kept at room temperature in a desiccator, it remained a turquoise color, but as soon as it was placed in the flask under nitrogen and heated, it turned black. Taha and Wilkinson (67) described the material as stable and polymeric. The polymeric conclusion was made on the basis of its low solubility. This work is in agreement with the stability of the black solid and that it has low solubility. An interaction between the species in the reaction mixture and nitrogen may have occurred, but any further speculation concerning this possibility has no basis in experimental evidence.

RHENIUM(V) CHLORIDE IN ACETONE WITH PYRIDINE

There are several references in the literature to reactions of pyridine and rhenium(V) chloride, but there remains some confusion concerning what products are formed and under what conditions. Johnson et al (27) reported that rhenium(V) chloride, dissolved in acetone, reacts with excess pyridine to form μ-oxodioxotetrachlorotetrakis(pyridine)-dirhenium(V), $Re_2O_3Cl_4(C_5H_5N)_4$. However, when Cotton et al. (29) attempted to duplicate the reaction it was found that fresh rhenium(V) chloride yielded only an unidentified product. The product was described as being insoluble in methylene chloride, contrary to the reports of Johnson et al (27). It was, therefore, not μ-oxodioxotetrachloro-tetrakis(pyridine)dirhenium(V), $Re_2O_3Cl_4(C_5H_5N)_4$, as expected. The

"aged" rhenium(V) chloride, dissolved in acetone, reacted with excess pyridine to form a mixture of dioxotetrakis(pyridine)rhenium(V) chloride dihydrate, $[ReO_2(C_5H_5N)_4]Cl \cdot 2H_2O$ and μ-oxodioxotetrachlorotetrakis-(pyridine)dirhenium(V), $Re_2O_3Cl_4(C_5H_5N)_4$.

Eastland (53) reinvestigated this reaction, taking care to use only anhydrous acetone and pyridine, and working in the glove box. In this case only dioxotetrakis(pyridine)rhenium(V) chloride dihydrate, $[ReO_2(C_5H_5N)_4]Cl \cdot 2H_2O$ was produced.

In this work, the pyridine reaction was reinvestigated in an attempt to clarify the conflicting results found in the literature. This led to investigations of other variables, of which the most important were the use of "aged" rhenium(V) chloride and relative quantities of the reagents used. Johnson et al. (27) found that the reaction

$$ReOCl_3[(C_6H_5)_3P]_2 + 6C_5H_5N + 3H_2O \longrightarrow [ReO_2(C_5H_5N)_4]Cl \cdot 2H_2O + 2C_5H_5N \cdot HCl + 2\,(C_6H_5)_3P$$

occurs in an excess of pyridine. The reaction

$$2ReOCl_3[(C_6H_5)_3P]_2 + 6C_5H_5N + H_2O \longrightarrow Re_2O_3Cl_4(C_5H_5N)_4 + 2C_5H_5N \cdot HCl + 4\,(C_6H_5)_3P$$

occurs with two moles of pyridine per mole of rhenium. It has also been shown (27)(58) that the addition of excess pyridine to μ-oxodioxotetrachlorotetrakis(pyridine)rhenium(V), $Re_2O_3Cl_4(C_5H_5N)_4$, results in the reaction,

$$Re_2O_3Cl_4(C_5H_5N)_4 + 6C_5H_5N + 5H_2O \longrightarrow 2\,[ReO_2(C_5H_5N)_4]Cl \cdot 2H_2O + 2C_5H_5N \cdot HCl.$$

It was reasonable to expect that an excess of pyridine would react with rhenium(V) chloride according to the reaction,

$$Re_2Cl_{10} + 8H_2O + 16C_5H_5N \longrightarrow 2\left[ReO_2(C_5H_5N)_4\right]Cl\cdot 2H_2O + 8C_5H_5N\cdot HCl$$

as had been found by Cotton et al. (29) and Eastland (53). In the current work, the outcome of the reaction was found to be the same if "aged" rhenium(V) chloride or fresh rhenium(V) chloride was used in the reaction with excess pyridine; that is, dioxotetrakis(pyridine)-rhenium(V) chloride dihydrate, $\left[ReO_2(C_5H_5N)_4\right]Cl\cdot 2H_2O$, was formed.

When a stoichiometric amount of pyridine was used with either fresh or "aged" rhenium(V) chloride, the result of the reaction was μ-oxodioxotetrachlorotetrakis(pyridine)dirhenium(V), $Re_2O_3(C_5H_5N)_4$. There was no observable quantity of dioxotetrakis(pyridine)rhenium(V) chloride dihydrate, $\left[ReO_2(C_5H_5N)_4\right]Cl\cdot 2H_2O$, produced. On the basis of these results it appears that a typographical error occurred in the paper of Johnson et al. (27). It should read that "1.5 milliliters of pyridine were reacted" instead of "15 milliliters of pyridine were reacted with 2.0 grams of rhenium(V) chloride."[1] If such an error had been made, then it is difficult to understand how Cotton et al. (29) were able to isolate any μ-oxodioxotetrachlorotetrakis(pyridine)-dirhenium(V), $Re_2O_3Cl_4(C_5H_5N)_4$, in the way that they did, because they were working with a 38-fold excess of pyridine. These observations do explain why Eastland (53) was unable to repeat the work of Johnson et al. (27).

---

[1] N. P. Johnson, F. I. M. Taha and G. Wilkinson, J. Chem. Soc., 2616 (1964).

Johnson et al. (27) and Cotton et al. (29) have discussed the infrared spectrum of these two compounds. They have assigned the absorption band at 825 cm^{-1} in the spectrum of dioxotetrakis(pyridine)rhenium(V) chloride dihydrate, $[ReO_2(C_5H_5N)_4]Cl \cdot 2H_2O$, to the <u>trans</u> O=Re=O vibration. Absorptions due to the rhenium-oxygen vibrations in μ-oxodioxotetrachlorotetrakis(pyridine)dirhenium(V), $Re_2O_3Cl_4(C_5H_5N)_4$, were assigned to bands which appear at 970 (ν Re=O) and a strong, broad band which appeared to be at least a triplet at 700 cm^{-1}, due to the bridging Re-O-Re group with pyridine out-of-plane deformations overlapping with it. Pyridine out-of-plane deformations in dioxotetrakis(pyridine)rhenium(V) appear as a doublet at 691 cm^{-1} and 701 cm^{-1}. The observations made during this research were in agreement with their assignment.

Every reaction between pyridine and rhenium(V) chloride initially produced a gray-green material. This was apparently the same material which Cotton et al. (29) observed in the reaction between fresh rhenium(V) chloride and pyridine. It does not dissolve in acetone, acetonitrile, ethanol, tetrahydrofuran, methylene chloride or chloroform. A portion of the gray-green solid does dissolve in dimethyl sulfoxide producing a green solution and a black residue. Recovery of a solid without decomposition has not been accomplished yet. Some of the gray-green solid also dissolves in pyridine resulting in a green solution and a black solid. Attempts to isolate a solid from the green solution produced an oil. The infrared spectrum of the gray-green solid suggested that pyridine was present in the solid. This was suggested by bands at 678 cm^{-1} and 741 cm^{-1} as well as bands at

1489 cm^{-1}, 1537 cm^{-1}, 1610 cm^{-1} and 1638 cm^{-1} which are near frequencies that have been suggested for coordinated pyridine (80)(81). The spectrum also has bands at 295 cm^{-1} and 331 cm^{-1} which would be indicative of rhenium-chlorine absorptions (59).

In conclusion, it was found that the most important factor in the successful preparation of μ-oxodioxotetrachlorotetrakis(pyridine)-dirhenium(V), $Re_2O_3Cl_4(C_5H_5N)_4$, was to limit the amount of pyridine which was used to amounts near the stoichiometric amount required for the reaction. The use of "aged" rhenium(V) chloride did not seem to improve the reaction, thus it was concluded that whether rhenium(V) chloride was "aged" or fresh was of little importance. This is probably because in the presence of water and a basic material, such as pyridine, rhenium(V) chloride will undergo hydrolysis without the benefit of the "aging" process.

SEALED TUBE REACTIONS

Leitheiser (47) has noted the importance of the solvent and the effect of its purity on reactions of oxotrichlorobis(triphenylphosphine)-rhenium(V), $ReOCl_3\left[(C_6H_5)_3P\right]_2$, at temperatures above the boiling point of the solvent. Work carried out since then by Losinski (82), Holm (83), and Gehrke (79) indicated inconsistencies. Therefore, it was decided to reinvestigate portions of this work.

Sealed Tube Reactions of Chloroform and Oxotrichlorobis(triphenylphosphine)rhenium(V)

Stock Chloroform

Gehrke (54) and Leitheiser (47) have described the reaction between

stock chloroform and oxotrichlorobis(triphenylphosphine)rhenium(V), $ReOCl_3\left[(C_6H_5)_3P\right]_2$. They found that two products were formed, tetrachlorobis(triphenylphosphine)rhenium(IV), $ReCl_4\left[(C_6H_5)_3P\right]_2$, and tetrachlorobis(triphenylphosphine oxide)rhenium(IV), $ReCl_4\left[(C_6H_5)_3PO\right]_2$. Tetrachlorobis(triphenylphosphine oxide)rhenium(IV), $ReCl_4\left[(C_6H_5)_3PO\right]_2$, was found to be the major product. The present work is in agreement with these findings. Leitheiser (47) studied the effect of time and temperature on the relative amounts of the two products. When a reaction time of fifteen hours and a temperature of 120°C was used, virtually no tetrachlorobis(triphenylphosphine)rhenium(IV), $ReCl_4\left[(C_6H_5)_3P\right]_2$, was formed. When the reaction time was five hours and the temperature was 110°C, the amount of tetrachlorobis(triphenylphosphine)rhenium(IV), $ReCl_4\left[(C_6H_5)_3P\right]_2$, was increased but never became the major product. Even at the lower temperature, when the reaction time was lengthened to about twelve hours, the yield of tetrachlorobis(triphenylphosphine oxide)rhenium(IV), $ReCl_4\left[(C_6H_5)_3PO\right]_2$, became nearly quantitative. Leitheiser (47) has considered the source of oxygen necessary to produce the triphenylphosphine oxide required for the complex. He concluded that it could come from dissolved oxygen, water or ethanol in the chloroform. These sources were in addition to the oxygen from oxotrichlorobis(triphenylphosphine)rhenium(V), $ReOCl_3\left[(C_6H_5)_3P\right]_2$, which was abstracted by triphenylphosphine. Chatt and Rowe (84) have shown that when oxotrichlorobis(triphenylphosphine)rhenium(V), $ReOCl_3\left[(C_6H_5)_3P\right]_2$, was heated with excess triphenylphosphine, oxygen

was removed giving trichlorotris(triphenylphosphine)rhenium(III), $ReCl_3[(C_6H_5)_3P]_3$, and triphenylphosphine oxide. Gehrke (54) has shown that prolonged boiling of oxotrichlorobis(triphenylphosphine)rhenium(V), $ReOCl_3[(C_6H_5)_3P]_2$, results in the formation of tetrachlorobis(triphenylphosphine)rhenium(IV), $ReCl_4[(C_6H_5)_3P]$, and triphenylphosphine oxide, which showed that the oxygen was removed. In order for this to occur, triphenylphosphine must first be liberated from the coordination sphere. Then a part of this triphenylphosphine would react with the oxygen on the rhenium, forming triphenylphosphine oxide which then forms the coordinate covalent bond with rhenium. Another part of the triphenylphosphine could react with another source of oxygen—dissolved oxygen, water or ethanol in the chloroform—forming triphenylphosphine oxide. The triphenylphosphine oxide thus produced would coordinate to the rhenium, forming tetrachlorobis(triphenylphosphine oxide)rhenium(IV), $ReCl_4[(C_6H_5)_3PO]_2$ (27)(78)(85). The additional chlorine required to form this complex would have to come from the solvent, chloroform.

When pure chloroform was used (47) and the tube was flushed with helium, the amount of tetrachlorobis(triphenylphosphine)rhenium(IV), $ReCl_4[(C_6H_5)_3P]_2$, was increased slightly to a yield of about 8%. The formation of 76% tetrachlorobis(triphenylphosphine oxide)rhenium(IV), $ReCl_4[(C_6H_5)_3PO]_2$, still required more oxygen than could be supplied by the oxygen available from the oxotrichlorobis(triphenylphosphine)-rhenium(V), $ReOCl_3[(C_6H_5)_3P]_2$. Thus there was still an additional source of oxygen required, perhaps dissolved oxygen in the solvent, chloroform.

Stock Chloroform with Excess Triphenylphosphine

It has been shown that one way to reduce the formation of triphenylphosphine oxide complexes is to use an excess of triphenylphosphine (75)(86). Leitheiser (47), using this rationale, used excess triphenylphosphine in an attempt to increase the yield of tetrachlorobis(triphenylphosphine)rhenium(IV), $ReCl_4[(C_6H_5)_3P]_2$. Instead, the reaction produced bis(methyltriphenylphosphonium)hexachlororhenate(IV), $[(C_6H_5)_3PCH_3]_2ReCl_6$, and a small amount of tetrachlorobis(triphenylphosphine)rhenium(IV), $ReCl_4[(C_6H_5)_3P]_2$, was produced. The results of the present research are in agreement with the formulation proposed by Leitheiser (47). This formulation was verified by direct combination of methyltriphenylphosphonium ion, $[(C_6H_5)_3\overset{+}{P}CH_3]$, and hexachlororhenate ion, $ReCl_6^{1-}$ (47). Infrared spectroscopy revealed a unique and diagnostic pair of absorption bands at 901 cm^{-1} and 889 cm^{-1} which are thought to be caused by the methyl group (87). In addition to this doublet there are also bands at 1414 cm^{-1} and 1327 cm^{-1} which are "an almost infallible indication of the presence of phosphorus-methyl groups in a phosphorus compound"[2]. The band near 1420 cm^{-1} (1414 cm^{-1} in this compound) is a weak band due to the asymmetric mode of the phosphorus-methyl group, and the band near 1300 cm^{-1} (1327 cm^{-1} in this compound) is a sharp band of moderate intensity due to the symmetrical absorption mode of the methyl group. The bands which occur at 295 cm^{-1} and 305 cm^{-1} are in close agreement with bands reported for the

[2] D. E. C. Corbridge, Topics in Phosphorus Chemistry, 6, 298(1969).

bis(tetraethylammonium)hexachlororhenate(IV), $\left[(C_2H_5)_4N\right]_2ReCl_6$, at 314 cm^{-1} and 300 cm^{-1} (59). Thus the evidence obtained by infrared spectroscopy is consistent with a formulation of bis(methyltriphenylphosphonium)hexachlororhenate(VI), $\left[(C_6H_5)_3PCH_3\right]_2ReCl_6$.

Table XXVI shows ways in which triphenylphosphine is known to react with some chlorinated hydrocarbons. The reaction sequence shown in Table XXVII provides a reasonable way in which, from the product of the bromoform reaction with triphenylphosphine (Table XXVI), the methyltriphenylphosphonium cation, $\left[(C_6H_5)_3\overset{+}{P}CH_3\right]$, could be produced (91)(92)(93)(94)(95)(96)(97).

The sequence of reactions is written for the case in which bromoform was used. That it is reasonable for the chlorine analogue is shown by the observation that dichloromethyltriphenylphosphonium bromide, $\left[(C_6H_5)_3PCHCl_2\right]Br$ does form (90) (Table XXVI). The reaction sequence may require that triphenylphosphine and chloroform be "activated" in order to react in an analogous way. Such "activation" is likely provided by the presence of oxotrichlorobis(triphenylphosphine)rhenium(V), $ReOCl_3\left[(C_6H_5)_3P\right]_2$, under conditions found in the sealed tube, as shown by the results of this research and the work of Leitheiser (47).

The sequence of reactions correctly accounts for the final formation of the methyltriphenylphosphonium cation, $\left[(C_6H_5)_3\overset{+}{P}CH_3\right]$, (VII in Table XXVII, page 127). The sequence also shows the source of the chlorine which is needed to produce the hexachlororhenate ion, $ReCl_6^{1-}$. This chlorine could easily be supplied by the dichloro(triphenylphosphine),

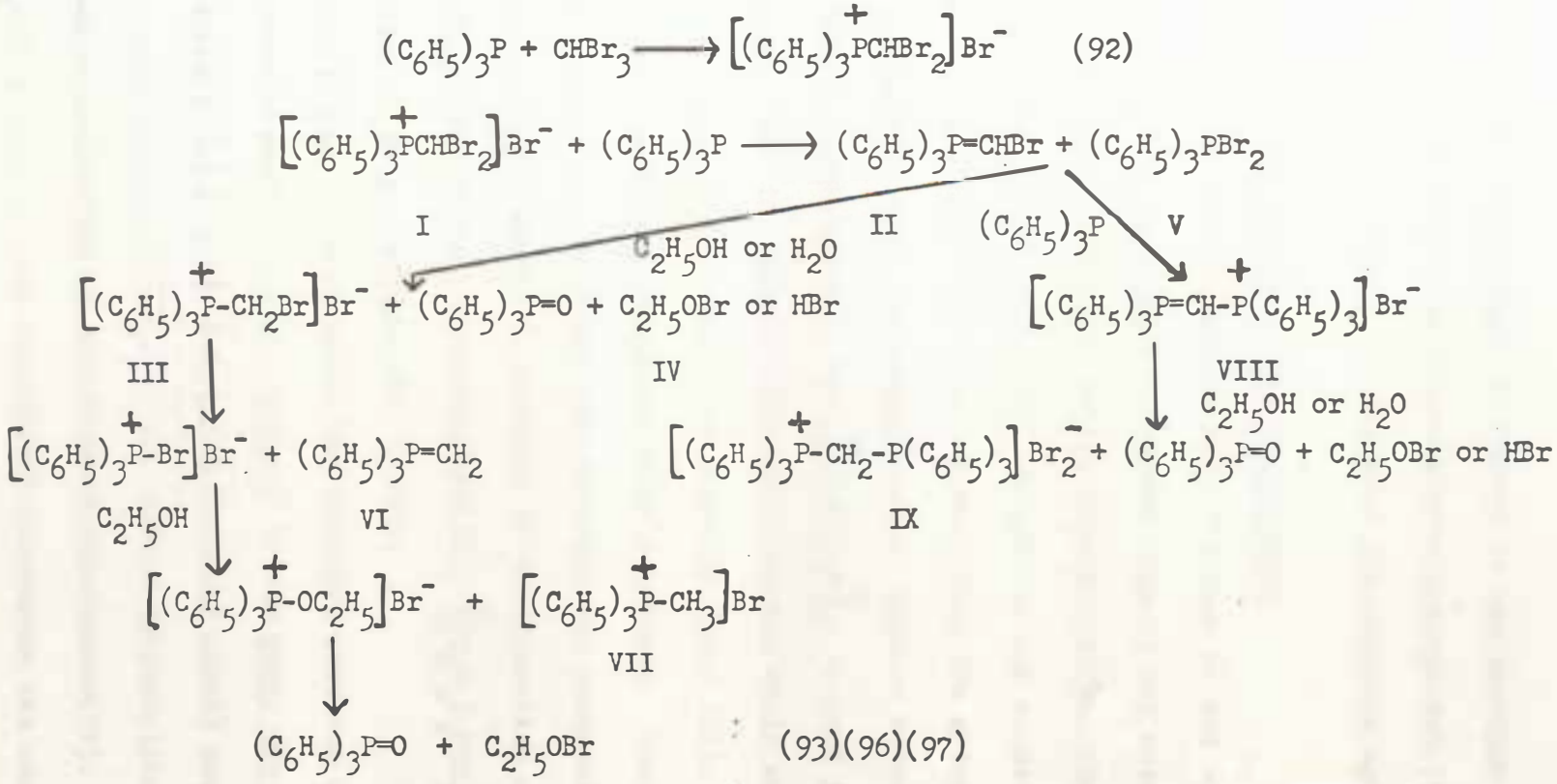
TABLE XXVI

REACTIONS OF TRIPHENYLPHOSPHINE
WITH CHLORINATED HYDROCARBONS

Chlorinated Hydrocarbon	Conditions of Reaction	Product(s)	Reference
CCl_4	Room Temperature Anhydrous	$(C_6H_5)_3PCl_2$ $(C_6H_5)_3P{=}CCl_2$	(88)
$CHCl_3$	62°C	No Rx	(89)
$CHCl_3$	120°C Sealed Tube	No Rx	(47)
$CHBr_3$	<150°C	$[(C_6H_5)_3PCHBr_2]Br$	(89)
$CHBr_2Cl$		$[(C_6H_5)_3PCHCl_2]Br$	(90)

TABLE XXVII

PROPOSED REACTION SEQUENCE



$(C_6H_5)_3PCl_2$ (V), moiety, which would be formed in the reaction sequence shown (Table XXVII, page 127). Dichloro(triphenylphosphine), $(C_6H_5)_3PCl_2$, has been shown (98)(88)(85) to be an efficient chlorinating agent.

Pure Chloroform with Excess Triphenylphosphine

Additional evidence which supports this sequence of reactions was obtained by purifying the chloroform to remove ethanol and water. Then the reaction was carried out between oxotrichlorobis(triphenylphosphine)rhenium(V), $ReOCl_3\left[(C_6H_5)_3P\right]_2$, pure chloroform and excess triphenylphosphine. With ethanol and water removed from the chloroform there was the possibility that the reaction might produce tetrachlorobis(triphenylphosphine)rhenium(IV), $ReCl_4\left[(C_6H_5)_3P\right]_2$, in good yield. If this did happen, then the excess triphenylphosphine would serve as was expected in the unpurified chloroform reaction (page 122), to retard the formation of triphenylphosphine oxide complexes. Instead of the anticipated reaction, an entirely new compound was produced. This showed that ethanol and/or water is involved in the formation of bis(methyltriphenylphosphonium)hexachlororhenate(IV), $\left[(C_6H_5)_3PCH_3\right]_2ReCl_6$. Further discussion of this reaction will follow.

Additional evidence which supports the proposed sequence of reactions was obtained by adding absolute ethanol to the pure, dry chloroform. The reaction between pure chloroform (ethanol added) oxotrichlorobis(triphenylphosphine)rhenium(V) and excess triphenylphosphine produced bis(methyltriphenylphosphonium)hexachlororhenate(IV), $\left[(C_6H_5)_3PCH_3\right]_2ReCl_6$, just as when unpurified chloroform was used.

The replacement of ethanol with other alcohols (propanol, butanol and 2-methyl butanol) in the chloroform resulted only in the formation of bis(methyltriphenylphosphonium)hexachlororhenate, $\left[(C_6H_5)_3PCH_3\right]_2ReCl_6$ (47).

On the other hand, a reaction in which water (7.6μl) was added to purified chloroform was expected to produce the same bis(methyltriphenylphosphonium)hexachlororhenate(IV), $\left[(C_6H_5)_3PCH_3\right]_2ReCl_6$, but it did not. Instead, a material was produced which showed evidence, in the infrared spectrum, of decomposition when recrystallization was attempted. Further characterization of this material was not attempted at the time because there was indication that water was not responsible for the formation of the cation. Further study of the possible reaction sequence suggests that there was perhaps not enough water present for the reaction to take place as expected. (7.6μl of water is about 0.42 mmol. To produce the methyl(triphenylphosphine) cation, $\left[(C_6H_5)_3\overset{+}{P}CH_3\right]$, in 0.6 mmol. of bis(methyltriphenylphosphonium)hexachlororhenate(IV), $\left[(C_6H_5)_3\overset{+}{P}CH_3\right]$, would require 1.2 mmol. of water).

1. Dichloromethyltriphenylphosphonium Pentachloro(triphenylphosphine oxide)rhenium(IV)

Return to the reaction of pure chloroform in which there were three species produced by the reaction between pure chloroform, excess triphenylphosphine and oxotrichlorobis(triphenylphosphine)rhenium(V), $ReOCl_3\left[(C_6H_5)_3P\right]_2$. These species were a green crystalline material, a white powder and a purple powder. Consider first the green material

which was formulated by Leitheiser (47) as dichloromethyltriphenylphosphonium pentachloro(triphenylphosphine oxide)rhenate(IV), $[(C_6H_5)_3PCHCl_2][ReCl_5(C_6H_5)_3PO]$. This compound could not be recrystallized without decomposition. Decomposition was suggested by changes in the infrared spectrum. Therefore, in order to obtain an elemental analysis the green crystals were separated mechanically, choosing only those which were the clearest green. The analysis which resulted from these crystals was consistent with the formulation dichloromethyltriphenylphosphonium pentachloro(triphenylphosphine oxide)rhenate(IV).

Analysis of the infrared spectrum was consistent with this formulation. A band at 290 cm^{-1} with additional structure can be attributed to rhenium-chlorine (59) absorption. Comparison with the rhenium-chlorine absorption found for 1,1-dimethyl-3-oxobutyltriphenylphosphonium pentachlorotriphenylphosphinerhenate (IV), $\left[CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-P(C_6H_5)_3\right] ReCl_5[(C_6H_5)_3P]$, which exhibits a rhenium-chlorine absorption at 311 cm^{-1}, suggests that 290 cm^{-1} is somewhat lower than might be expected (53) for an $[ReCl_5L]^-$ anion. The shoulder at 538 cm^{-1} could be due to the x-sensitive mode (an absorption mode which is due to the species attached to the phenyl ring) of coordinated triphenylphosphine oxide (72)(73)(74). Absorption bands at 611 cm^{-1} and 621 cm^{-1} are possibly due to carbon-chlorine absorptions (100) of a $-CHCl_2$ moiety. Infrared absorption due to carbon-carbon bonds in triphenylphosphine systems occur at 685 cm^{-1} (72)(73)(74). An x-sensitive absorption of either triphenylphosphine oxide and/or a

triphenylphosphonium moiety appears at 729 cm^{-1} (72)(74)(75). This assignment is consistent with bands which appear in that region for known phosphonium salts, as observed by Eastland (53). The band at 1110 cm^{-1} is possibly due to the x-sensitive mode of co-ordinated triphenylphosphine oxide and the triphenylphosphonium salt (72)(73)(74)(53).

Until the green material can be successfully recrystallized and elemental analysis obtained on recrystallized samples, the proposed formulation, dichloromethyltriphenylphosphonium pentachloro(triphenylphosphine oxide)rhenate(IV), $\left[(C_6H_5)_3PCHCl_2\right]\ ReCl_5\left[(C_6H_5)_3PO\right]$, can only be regarded as tentative. Reference to the reaction sequences which were discussed beginning on page 125, does provide support for the proposed formulation. In the absence of water and ethanol the sequence could be expected to terminate at product VIII. An equilibrium between product V and products I and II would provide the cation which is required by this formulation. Again, this accounts for the chloride ion necessary for the formation of the pentachloro(triphenylphosphine oxide) rhenate anion, $ReCl_5\left[(C_6H_5)_3PO\right]^-$.

Triphenylphosphine oxide could be generated either by direct interaction of triphenylphosphine with the oxygen of the oxotrichlorobis-(triphenylphosphine)rhenium(V), $ReOCl_3\left[(C_6H_5)_3P\right]_2$, or the ylide, $(C_6H_5)_3P{=}CHCl$, might interact with oxygen to form triphenylphosphine oxide. The unstable nature of this complex was illustrated by consideration of the infrared spectrum of the material after recrystallization was attempted. A band which is due to rhenium-chlorine absorptions was shifted from 290 cm^{-1} to 305 cm^{-1} and became one band instead

of the three or four bands found in the spectrum prior to recrystallization. The bands at 611 cm^{-1} and 621 cm^{-1} change intensity relative to one another and to bands at 524 cm^{-1} and 539 cm^{-1}. Bands at 590 cm^{-1} and 620 cm^{-1} disappear entirely and a band appears at 989 cm^{-1} while one band disappears at 900 cm^{-1}. A band at 1110 cm^{-1} is replaced by bands at 1090 cm^{-1}, 1124 cm^{-1} and 1150 cm^{-1}. Changes which occurred in the infrared spectrum after recrystallization suggested the formation of coordinated triphenylphosphine oxide. This was suggested by bands which appear at 690 cm^{-1}, 728 cm^{-1} and 748 cm^{-1}. These bands, with the most intense being the central band, are typical of coordinated triphenylphosphine oxide. Similarly, the bands which appeared between 1090 cm^{-1} and 1150 cm^{-1} suggested coordinated triphenylphosphine oxide. The spectrum further suggested that what remained was no longer a salt. This was indicated by the loss of fine structure in the bands between 690 cm^{-1} and 750 cm^{-1}. This correlation was suggested by comparing spectra for known triphenylphosphonium salts to the spectra of coordinated triphenylphosphine and coordinated triphenylphosphine oxide.

A second possible formulation of the green material was suggested by examination of the proposed sequence (Table XXVII, page 127). This examination suggested that chloromethylenebis(triphenylphosphonium)-hexachlororhenate(IV), $\left[(C_6H_5)_3P\text{-}\underset{\displaystyle H}{\overset{\displaystyle Cl}{\underset{|}{\overset{|}{C}}}}\text{-}P(C_6H_5)_3\right]ReCl_6$, might be a reasonable formulation. Theoretical elemental analysis for this product (Re 19.13%; Cl 25.52%; P 6.36%; C 45.67%; H 3.31%) gives a somewhat

better correlation between the experimental results (Re 19.15%; Cl 25.62%; P 6.20%; C 45.25%; H 3.27%) and the theoretical than did the theoretical analysis for dichloromethyltriphenylphosphonium pentachloro(triphenylphosphine oxide)rhenate (IV) (Re 18.85%; Cl 25.12%; P 6.27%; C 44.96%; H 3.16%).

Analysis of the infrared spectrum based on chloromethylbis(triphenylphosphonium) hexachlororhenate(IV), $\left[(C_6H_5)_3P\text{-}\underset{\underset{H}{|}}{\overset{\overset{Cl}{|}}{C}}\text{-}P(C_6H_5)_3\right]ReCl_6$, shows a band at 290 cm^{-1} with a shoulder at 280 cm^{-1} and another shoulder at 304 cm^{-1} which compares well with that found by Eastland (53) for bis[1,1-dimethyl-3-oxobuty(triphenylphosphonium)] hexachlororhenate (IV), $\left[CH_3\text{-}\overset{\overset{O}{\|}}{C}\text{-}CH_2\text{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{-}P(C_6H_5)_3\right]_2ReCl_6$, in which the rhenium-chlorine absorption frequencies were found at 294 cm^{-1} as a very strong absorption with a shoulder at 275 cm^{-1} and another shoulder at 302 cm^{-1}. Absorption bands at 611 cm^{-1} and 621 cm^{-1} could be due to carbon-chlorine absorptions of a $\text{-}\underset{\underset{Cl}{|}}{\overset{\overset{H}{|}}{C}}\text{-}$ moiety, although it is not possible to distinguish between a $\text{-}\underset{\underset{Cl}{|}}{\overset{\overset{H}{|}}{C}}\text{-}$ moiety and a $-CHCl_2$ group from the infrared. The bands which appear between 680 cm^{-1} and 770 cm^{-1} are very similar in complexity to the bands which appear in the same region of the bis(methyltriphenylphosphonium) hexachlororhenate, $\left[CH_3P(C_6H_5)_3\right]_2ReCl_6$. (Compare

Figure 34, page 167 with Figure 47, page 171). A similar comparison of the bands which occur at or near 1110 cm^{-1} in the above figures shows the similarity of those bands. The band shape is also apparently different between triphenylphosphine oxide complexes and triphenylphosphonium salts $\left[RP(C_6H_5)_3\right]$. When R is methyl, phenyl or 1,1-dimethyl-3-oxobutyl (53), a single strong, sharp absorption is found near 1110 cm^{-1}, while in triphenylphosphine oxide complexes there are generally three bands, which tend to be broader bands (72).

Still the choice between the proposed formulations dichloromethyltriphenylphosphonium pentachloro(triphenylphosphine oxide)rhenate(IV), $\left[CHCl_2P(C_6H_5)_3\right]$ $ReCl_5\left[(C_6H_5)_3PO\right]$, and chloromethylenebis(triphenylphosphonium) hexachlororhenate, $\left[(C_6H_5)_3P\text{-}\underset{Cl}{\overset{H}{C}}\text{-}P(C_6H_5)_3\right]ReCl_6$, cannot be made without further information which might be obtained by direct interaction of the ions involved. Unfortunately, the dichloromethyltriphenylphosphonium salt does not appear in the proposed scheme at a reasonable stopping place. On the other hand, the chloromethylenebis(triphenylphosphonium) salt requires that Compound (V) (Table XXVII, page 127), be chlorinated. At the present time it is proposed that chloromethylbis(triphenylphosphonium) cation, $(C_6H_5)_3P\text{-}\underset{H}{\overset{Cl}{C}}\text{-}P(C_6H_5)_3$, would come from compound (II) (Table XXVII, page 127), by loss of hydrogen rather than loss of the halogen.

2. White Powder

A second material formed by the reaction between pure chloroform, oxotrichlorobis(triphenylphosphine)rhenium(V), $ReOCl_3[(C_6H_5)_3P]_2$, and excess triphenylphosphine was a white powder. Because of the complexity of the discussion involving this material, the discussion will use the following outline: a) Unrecrystallized Material, b) Recrystallized Material, c) Recrystallized Material Heated at Reduced Pressure, d) Recrystallized Material Heated at One Atmosphere, e) Derivatives of the Recrystallized Material and f) Formulation of the Recrystallized White Powder.

Leitheiser (47) proposed the formulation dichloromethyltriphenylphosphonium chloride, $[(C_6H_5)_3PCHCl_2]Cl$, as a logical outgrowth of the formation of the green material. He proposed the formulation, dichloromethyltriphenylphosphonium pentachloro(triphenylphosphine oxide)rhenate (IV), $[(C_6H_5)_3PCHCl_2][ReCl_5(C_6H_5)_3PO]$, for the green material. The formulation for the white powder has become suspect, as will be shown in subsequent sections.

a) Unrecrystallized Material

The data obtained for the white material was outlined in Table XX, page 66. The unrecrystallized material was found to contain 24.47% chlorine with 10.89% in the form of ionic chlorine. The proposed formulation of Leitheiser (47) requires a total chlorine of 27.89% and an ionic chlorine content of 9.29%.

The mass spectrum of the material indicates that the unrecrystallized material contains some chloroform. Evidence suggests that this

is entrapped chloroform, because it appears as the sample is heated to introduce it into the ionization chamber of the mass spectrometer. No fragments appear at higher masses at the temperature of the inlet probe at which the chloroform appears. The chlorcform appears at mass numbers of 117, 119, 121 and 123. This indicates that the chloroform is not a part of the material, except as either a loosely bound or entrapped species.

Analysis of the infrared spectrum of the unrecrystallized material reveals bands between 685 cm^{-1} and 850 cm^{-1} which suggest a triphenylphosphine or triphenylphosphonium formulation, as proposed. This is indicated by the presence of two strong bands bracketing a band of weak-to-moderate intensity typical of triphenylphosphine (72) complexes and sometimes of triphenylphosphonium salts (53). A band at 1110 cm^{-1} with a shoulder at 1104 cm^{-1} adds further evidence to the idea that the material is a phosphonium salt. However, there is no evidence for a $-CHCl_2$ moiety in the expected region between 580 cm^{-1} and 620 cm^{-1}. The infrared spectrum also exhibited bands at 2675 cm^{-1}, 2765 cm^{-1}, 3420 cm^{-1} and 3480 cm^{-1}, which cannot be accounted for on the basis of the proposed dichloromethyltriphenylphosphonium chloride, $[(C_6H_5)_3PCHCl_2]Cl$, formulation. The bands at 3420 cm^{-1} and 3480 cm^{-1} could be accounted for by water and/or ethanol except that they are present even in the crude sample which was only contacted by pure chloroform and worked up in the glove box. Though traces of ethanol and/or water might be present either in the glove box atmosphere or in the chloroform, the inclusion of water or ethanol in the material

would still not account for the bands observed at 2675 cm^{-1} and 2765 cm^{-1}. Even if water or ethanol were responsible for these bands, the analysis would still be inconsistent with dichloromethyltriphenylphosphonium chloride, $[CHCl_2P(C_6H_5)_3]Cl$, as a formulation.

b) Recrystallized Material

Recrystallization was accomplished from ethanol and diethyl ether. After recrystallization, the analysis, as indicated in Table XX, page 66, showed 11.41% total chlorine and 10.80% ionic chlorine. A carbon and hydrogen analysis did not fit this formulation either. This raised considerable doubt about the proposed formulation of the white material. However, it still appeared that it was a salt. Analysis by mass spectroscopy showed no evidence for entrapped chloroform nor was it possible to detect a molecular ion. (The instrument used was capable of the mass range from 0-500 mass units). Thus, the molecular mass was above 500 mass units, not 381 as the proposed formulation required. The infrared spectrum of the recrystallized material was identical to that of the unrecrystallized material (Compare Figure 37, page 168, with Figure 38, page 168).

c) Recrystallized Material Heated at Reduced Pressure

When a sample was to be analyzed it was heated overnight in an Abderhalden drying pistol at 80° and 0.1 torr. Heating the recrystallized white material resulted in some subtle changes, particularly in the infrared spectrum, which suggest some decomposition. Analysis of this material was reasonably consistent with the recrystallized,

unheated material, as a comparison of the data tabulated in Table XX, page 66, will show. Mass spectroscopic analysis performed at the University of Wyoming indicated that the molecular mass of the material was 538 mass units rather than the expected value, 381 mass units.

A molecular mass determination obtained by vapor pressure osmometry indicated a molecular mass of 276 in a solution of 85.06 milligrams of the white powder in 10 milliliters of ethanol, while a molecular mass of 216 was indicated for a solution of 34.61 milligrams of the powder in 10 milliliters. This data is indicative of an incompletely dissociated salt. The data was subjected to graphical analysis and a straight line was constructed. Extrapolation of the straight line to infinite dilution indicated a molecular mass of 179. If the salt is a uni-univalent salt, the formula mass of salt would be 348, based on vapor pressure osmometer data, compared to 381 for the proposed structure. If the salt is a di-univalent or uni-divalent salt, then the formula mass would be 537, based on vapor pressure osmometer data.

Changes in the infrared spectrum were subtle. A band appeared at 530 cm^{-1}, while a band centered at 740 cm^{-1} broadened. The most noticeable changes occurred above 2000 cm^{-1}, where bands became weaker and broader, particularly between 2600 cm^{-1} and 2800 cm^{-1} and 3300 cm^{-1} and 3600 cm^{-1}. A new band was observed at 2908 cm^{-1}. These observations suggest that decomposition had occurred.

d) Recrystallized Material Heated at One Atmosphere Pressure

Heating the white material at one atmosphere and 140° caused extensive changes in the infrared spectrum. The changes are vividly

shown by reference to the spectrum (Figure 40, page 169).

e) Derivatives of the Recrystallized Material

The infrared spectrum of the tetrakis(thiocyanato)diaminechromate (III) derivative of the white powder, $\left[Cr(NH_3)_2(SCN)_4\right]^{1-}$, seemed to indicate that further analysis would be useful. A carbon and hydrogen analysis was obtained, giving 49.54% C and 3.52% H. That is in poor agreement with dichloromethyltriphenylphosphonium tetrakis(thiocyanato-diamminechromate(III), $\left[(C_6H_5)_3PCHCl_2\right]\left[Cr(NH_3)_2(SCN)_4\right]$, which requires a carbon analysis of 41.57% and a hydrogen analysis of 4.66%. Differences between the theoretical and the empirical values could be due to impurities in the sample analyzed, the size of the sample analyzed or to an incorrect formulation. The tetraphenylborate and perrhenate derivatives of the white powder gave infrared spectra which indicated that gross changes had occurred and they were not considered further. These changes could have occurred as a result of more extensive reactions than the expected double replacement reactions.

f) Formulation of the Recrystallized White Powder

Previously, the result of various experiments were described. It is now appropriate to consider the possibilities which these results suggest.

(1) Dichloromethyl (triphenylphosphonium) chloride

Dichloromethyl (triphenylphosphonium) chloride, $\left[(C_6H_5)_3PCHCl_2\right]Cl$, the previously proposed formulation (47), has been shown to be an incorrect formulation.

(2) Chloroform Adduct

A possible formulation was suggested by work reported by Arzoumanidis (100) which would include chloroform as a part of the formulation. A formulation such as, $[(C_6H_5)_3PCl_2] \cdot 2CHCl_3$, would satisfy the mass spectroscopic data obtained from the unrecrystallized material. However, this compound requires 39.2% chlorine while the empirical value for the total chlorine content was 24.47%. Furthermore, this compound would not account for the observed infrared absorptions above 2000 cm^{-1}. Thus, except for the mass spectral data, the evidence available does not encourage further consideration of this possibility.

(3) Dihydroxymethyltriphenylphosphonium chloride

This possibility was considered because it satisfies the elemental analysis and it also explains certain features of the infrared spectrum. Dihydroxymethyltriphenylphosphonium chloride, $\left[(C_6H_5)_3PC(OH)_2H\right]Cl$, requires 10.6% chlorine. The hydroxy groups would explain the spectral evidence found at 3420 cm^{-1} and 3480 cm^{-1} (78). However, no support for such a formulation can be found in the literature. Discussions with Gehrke (101) and Worman (102) have suggested that this compound would be hydrolytically unstable and immediately decompose to triphenylphosphine oxide. Furthermore, none of the molecular mass data supports this formulation. The probable hydrolytic instability of this moiety, as well as the mass spectroscopic data, suggested that further consideration of this formulation would not be worthwhile.

(4) Methylenebis(triphenylphosphonium chloride)

Consideration of the reaction sequence (Table XXVII, page 127), which suggested a route by which other compounds in this series of reactions might be explained, suggested that methylenebis(triphenylphosphonium chloride), $\left[(C_6H_5)_3P\text{-}CH_2\text{-}P(C_6H_5)_3\right]Cl_2$, (94)(103)(104)(105)(106)(107) would be a reasonable possibility. This formulation agrees with mass spectral data (Page 138) which suggests a mass of 535 mass units. This mass would not come directly from methylenebis(triphenylphosphonium chloride), because the cation requires a mass of 538, but it is a doubly positive species, so the mass spectrum would indicate a peak at 269 rather than at 538. However, when methylenebis(triphenylphosphonium chloride), $\left[(C_6H_5)_3PCH_2P(C_6H_5)_3\right]Cl_2$ is heated, methylidebis(triphenylphosphorane), $(C_6H_5)_3P{=}C{=}P(C_6H_5)_3$, is formed (105). This moiety has a molecular mass of 536.6, in good agreement with the mass spectral data.

Vapor pressure osmometry suggested a molecular mass of 179 when extrapolated to infinite dilution. Methylenebis(triphenylphosphonium chloride), $\left[(C_6H_5)_3P\text{-}CH_2\text{-}P(C_6H_5)_3\right]Cl_2$, would ideally form three particles in solution. That suggests a molecular mass of 537 (required formula mass 605) from the vapor pressure osmometric data, which is consistent with the proposed structure, but the error is larger than desirable.

Infrared analysis, as was pointed out, revealed absorption bands which are unusual. The proposed methylenebis(triphenylphosphonium chloride), $\left[(C_6H_5)_3P\text{-}CH_2\text{-}P(C_6H_5)_3\right]Cl_2$, would have predicted bands at

frequencies near 818 cm^{-1} and 830 cm^{-1} (104)(105) due to the P-CH_2-P moiety. The spectrum had bands at 806 cm^{-1} and 821 cm^{-1}. An intense band was predicted near 1105 cm^{-1} (105) due to the x-sensitive mode of the phosphorus, and the spectrum had a band at 1110 cm^{-1}. Bands are predicted near 2600 cm^{-1} (105) which are due to carbon-hydrogen absorptions of the methylene group, and bands were observed at 2675 cm^{-1} and 2760 cm^{-1}. If the compound which was formed was either a hydrate or contained ethanol from recrystallization, the bands which were observed at 3420 cm^{-1} and 3480 cm^{-1} (78) would be expected. When the material was heated, changes occurred in the spectrum. The most notable of these was the disappearance of the bands at 2675 cm^{-1}, 2760 cm^{-1}, 3420 cm^{-1} and 3480 cm^{-1}. This could have been caused by the loss of the water of hydration (105) or loss of ethanol of crystallization (104) and dehydrochlorination (105). Other parts of the spectrum suggested that the sample was no longer pure and were, therefore, of little diagnostic value.

Reference to the reaction sequence (Table XXVII, page 127) revealed that water or ethanol would be necessary for the formation of the proposed compound. In one trial, care was taken to eliminate water and ethanol by using purified chloroform in the workup of the reaction mixture and the workup was done in the glove box. Still, there may have been traces of water and/or ethanol in the chloroform. Theoretical analysis of this proposed compound was not in complete agreement with the experimental results (Theoretical for $C_{37}H_{32}P_2Cl_2$: Cl 11.63%; P 10.16%; C 72.91%; H 5.29%. Found: Cl 10.54%; P 9.45%; C 68.44%; H 5.93%). If it was assumed that the compound existed as a monohydrate,

which was shown to be reasonable by Driscoll et al. (105), the analysis required for $C_{37}H_{34}P_2Cl_2O$ was: Cl 11.30%; P 9.87%; C 70.82%; H 5.46%. If it was assumed that the compound contained ethanol of crystallization, as shown by Driscoll et al.(105), then the theoretical for $C_{39}H_{38}P_2Cl_2O$ was: Cl 10.81%; P 9.45%; C 71.45%; H 5.84%. The empirical data suggest that there may have been impurities in the compound or decomposition may have occurred.

Methylenebis(triphenylphosphonium) bis {tetrakis(thiocyanato)-diamminechromate(III)} , $\left[(C_6H_5)_3PCH_2P(C_6H_5)_3\right]\left[Cr(NH_3)(SCN)_4\right]_2$, requires a carbon analysis of 45.99% and a hydrogen analysis of 3.77%. Empirically determined carbon content was 49.54% and hydrogen was 3.52%. If ethanol of crystallization was assumed to be present, the analysis required would be carbon 46.22% and hydrogen 4.12%. Only a small sample of the derivative was available, so replicate analyses were not possible. Since some temperature sensitivity had been observed with the parent salt, the sample was not dried prior to its analysis. Therefore, there was a possibility that some solvent remained in the sample which was analyzed.

In conclusion, the white material and the data obtained for it suggest a possible formulation as methylene(bistriphenylphosphonium chloride) hydrate, $\left[(C_6H_5)_3P\text{-}CH_2\text{-}P(C_6H_5)_3\right]Cl_2\cdot H_2O$, except that the analysis does not entirely fit this formulation. Further work is required to make a more positive identification of the compound or mixture of compounds.

(3) Purple Product of Reaction of Oxotrichlorobis(triphenylphosphine)rhenium(V) with Chloroform

The purple powder formed in this reaction was recovered in only very small amounts. Only after several trials of the reaction was enough accumulated to be able to obtain analysis. As a result, the conclusions on this compound are very tentative. The analyses which were obtained were not very consistent, perhaps because only limited amounts of sample were available. For example, the carbon analysis indicated 48.11% at one time and 47.59% at another time. Chlorine analysis gave 18.56% at one time and 19.53% another time. Rhenium analysis, 21.46%, was made on only one sample. It thus became very difficult to attempt to eludicate the structure. The infrared spectrum suggested a phosphine-phosphine oxide due to the series of bands between 1200 cm^{-1} and 1050 cm^{-1} (73)(74). The band at 1250 cm^{-1} could be due to a phosphorus-carbon phosphorus (87). This suggests that the compound might be methylenebis(triphenylphosphonium) bispentachloro-(triphenylphosphine oxide)rhenium(IV), $\left[(C_6H_5)_3P\text{-}CH_2\text{-}P(C_6H_5)_3\right]\left[ReCl_5(C_6H_5)_3PO\right]_2$. While the analysis fits well for carbon and hydrogen, it is less accurate for rhenium and chlorine (Theoretical for $Re_2Cl_{10}C_{73}H_{62}P_4O_2$: Re 20.43%; Cl 19.45%; C 48.12%; H 3.42%. Found: Re 21.46%; Cl 18.56%; C 48.11%; H 3.15%). A formulation based on the possible presence of the $Re_2Cl_8^{2-}$ anion was suggested by the purple color of the complex (53). In this case, analysis for rhenium and hydrogen fits well, but is less desirable for carbon and chlorine. (Theoretical for $Re_2Cl_8C_{73}H_{62}P_4O_2$: Re 21.27%; Cl 16.20%; C 50.07%;

H 3.57%). Another formulation based on the $Re_2Cl_9^{2-}$ anion does not fit any of the analyses. (Theoretical for $Re_2Cl_9C_{73}H_{62}P_4O_2$: Re 20.84%; Cl 17.86%; C 47.07%; H 3.50%).

Sealed Tube Reaction of Oxotrichlorobis(triphenylphosphine)rhenium(V) with Acetone

Leitheiser (47) has reported that this reaction produced dichlorotris(triphenylphosphine oxide) acetone rhenium(II), $ReCl_2[(C_6H_5)_3PO]_3(CH_3\overset{O}{\overset{\|}{C}}CH_3)$. This compound was isolated, after the concentrated mother liquor was allowed to stand about two weeks, as large, dark blue crystals which exhibited a carbonyl band in the infrared spectrum. Repeated attempts to reproduce this compound were unsuccessful. When unpurified acetone was used, an oil was produced which became an intractable material with which to work. When purified acetone was used, a similar oil was produced. Further work seemed futile and this reaction was abandoned.

Sealed Tube Reaction of Oxotrichlorobis(triphenylphosphine oxide) rhenium(V) with 2-butananone

The reaction of oxotrichlorobis(triphenylphosphine oxide)rhenium(V) with 2-butanone was one of the series of reactions designed to show how the solvent affects the course of the reaction. The results of this reaction show that blue trichloro(triphenylphosphine oxide)rhenium(III) was formed together with traces of what appeared to be tetrachlorobis-(triphenylphosphine)rhenium(IV) and a green material which was found only in low yield. Insufficient quantity of this material was

available to obtain elemental analysis. The formulation of the blue compound was in agreement with the findings of Leitheiser (47).

It was found that only 2-butanone obtained from Matheson, Coleman and Bell would allow the reaction to proceed. 2-butanone obtained from other sources produced only a very small amount of trichloro(triphenylphosphine oxide)rhenium(III), $ReCl_3\left[(C_6H_5)_3PO\right]$, which suggested that some impurity was responsible for the reaction. Gas chromatographic separation of the components of 2-butanone from Matheson, Coleman and Bell and from J. T. Baker produced superimpossible recorder tracings of three or four components (there was a possibility of incomplete resolution of the components). This makes it very difficult to explain why the reagent from one source behaves differently than from another.

In the purification of trichloro(triphenylphosphine oxide)rhenium(III), $ReCl_3\left[(C_6H_5)_3PO\right]$, the aluminum oxide used to separate the components must be acidic or the complex will decompose. After separation of the components the blue trichloro(triphenylphosphine oxide)rhenium(III), $ReCl_3\left[(C_6H_5)_3PO\right]$, must be recrystallized at least four times to obtain acceptable elemental analysis.

While the formulation, trichloro(triphenylphosphine oxide)rhenium(III), $ReCl_3\left[(C_6H_5)_3PO\right]$, fits the empirical elemental analysis, the infrared spectrum reveals two regions which contain bands which are atypical of triphenylphosphine oxide complexes. These regions are 1080 cm^{-1} to 1175 cm^{-1} and 1400 cm^{-1} to 1500 cm^{-1}. The region from 1080 cm^{-1} to 1175 cm^{-1} typically exhibits two or three bands, but the spectrum for this compound has three bands and a prominent shoulder. In the region from 1400 cm^{-1}

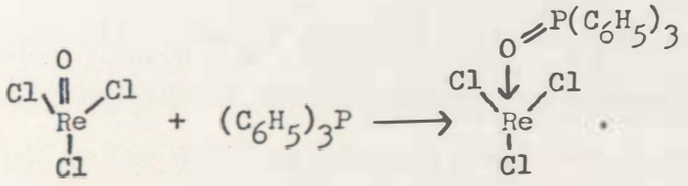
to 1500 cm^{-1} is typically found a strong band near 1445 cm^{-1} along with a moderate band at 1488 cm^{-1}. The infrared spectrum of this compound exhibits two strong bands, one at 1445 cm^{-1}, as expected, and a second band at 1458 cm^{-1} which is not typical of coordinated triphenylphosphine oxide. The infrared spectrum and analysis do not suggest an alternative formulation which would be consistent with the observed spectrum.

Electronic spectroscopy revealed absorption bands at 422 nanometers, 570 nanometers and 625 nanometers. Rhenium(III) complexes are known to exist in three different ways: 1) mononuclear complexes, in which there is one rhenium atom per complex; 2) dinuclear complexes; and 3) trinuclear complexes. The latter two would have two and three rhenium atoms, respectively, per complex. The electronic spectrum has been found to be diagnostic of dinuclear and trinuclear complexes of rhenium(III). It has been shown that dinuclear rhenium complexes absorb near 710 nanometers and 530 nanometers (53)(108). Trinuclear species have been found to absorb in the 751-813 nanometer range and the 515-571 nanometer range. The compound produced in this reaction absorbed at 625, 570 and 420 nanometers. Thus, it was not a multinuclear complex.

Formation of a phosphine oxide complex at temperatures above the boiling point of 2-butanone in sealed tubes suggested that a reaction of the following type occurred:

$$ReOCl_3\left[(C_6H_5)_3P\right]_2 \longrightarrow \left[ReOCl_3\right] + 2(C_6H_5)_3P$$

followed by



The liberated triphenylphosphine could also react with dissolved oxygen in the solution to form triphenylphosphine oxide which could then coordinate to the rhenium, giving the observed complex.

SUMMARY

This work has shown that the infrared spectra which are reported in the literature (20)(21) are more consistent with the infrared spectrum of oxotetrachlororhenium(VI) than rhenium(V) chloride. The oxotetrachlororhenium(VI) is produced together with rhenium(V) chloride by oxygen which is present during the chlorination of rhenium and may come from the chlorine used. After extensive purification of the rhenium(V) chloride, an infrared spectrum of that compound was obtained which is more representative than are the infrared spectra reported in the literature (20)(21).

It has been shown that carbon tetrachloride, chloroform and cyclohexane dissolve a very small amount or no rhenium(V) chloride at room temperature. It was observed that the solute which was recovered from these solutions would not melt at temperatures up to 350°C. After subjecting the recovered solute to a temperature of 350°C, it was found to be rhenium(III) chloride. Considerations of the source of the rhenium(III) chloride led to the suggestion that a small, but undetermined, amount of rhenium(V) chloride dissolves in these solvents.

Oxotetrachlororhenium(VI) was shown by electronic spectroscopy and reaction with triphenylphosphine to be present in solutions of carbon tetrachloride and rhenium(V) chloride. Reaction of oxotetrachlororhenium(VI) and triphenylphosphine in carbon tetrachloride produces tetrachloro(triphenylphosphinetriphenylphosphine oxide)rhenium(IV). A trans configuration of the triphenylphosphine and triphenylphosphine

oxide ligand is proposed. This proposal is based on the x-ray crystal structure (76) which showed that, in the monomer of oxotetrachlororhenium(VI) the vacant octahedral site is trans to the oxygen.

In work with other solvents it was found that 1,4-dioxane reacts with rhenium(V) chloride to form tetrachlorobis(1,4-dioxane)rhenium(IV), in agreement with observations of Allen et al.(31). Diethyl ether reacts with rhenium(V) chloride producing a material which infrared spectroscopy suggests is tetrachlorobis(diethyl ether). The material, however, is an oil and was not further characterized. Acetone reacts with rhenium(V) chloride producing an intractable oil. Acetone which was removed from the solute showed no evidence for the formation of 1,1-dimethyl-3-butene-2-one as was expected from the work of Eastland (53).

Studies of "aged" rhenium(V) chloride suggest that the "aging" process involves the hydrolysis of rhenium(V) chloride. The main evidence for this conclusion was found in the infrared spectrum, which indicated that rhenium dioxide and the perrhenate ion were present. X-ray powder photographs became more diffuse, which suggests some reaction such as hydrolysis.

The reaction between acetic acid-acetic anhydride and rhenium(V) chloride produces a material which contains no chlorine, while considerable rhenium is present. This is in conflict with the results observed by Taha and Wilkinson (67) where trichlorodiacetatorhenium(V) was found. The results obtained in this work suggested that rhenium dioxide, the perrhenate ion and other unknown species are present in the residue of the reaction.

This research has shown that excess pyridine reacts with an acetone solution of rhenium(V) chloride or "aged" rhenium(V) chloride to form dioxotetrakis(pyridine)rhenium(V) chloride dihydrate. When the stoichiometric amount of pyridine is used, the reaction with an acetone solution of rhenium(V) chloride or "aged" rhenium(V) chloride produces μ-oxodioxotetrachlorotetrakis(pyridine)rhenium(V). In addition, all reactions between an acetone solution of rhenium(V) chloride and pyridine produce a solid immediately upon adding the pyridine. This solid contains rhenium dioxide and another uncharacterized material. The most important condition for the reactions is the amount of pyridine; not whether "aged" rhenium(V) chloride is used.

A series of reactions between oxotrichlorobis(triphenylphosphine)-rhenium(V) and chloroform was carried out in sealed tubes. The reactions which occur produce products which are correlated well by a proposed reaction sequence based on the reaction of triphenylphosphine with chloroform. This sequence of reactions explains the formation of tetrachlorobis(triphenylphosphine oxide)rhenium(IV) in preference to tetrachlorobis(triphenylphosphine)rhenium(IV) in the reaction of stock chloroform with oxotrichlorobis(triphenylphosphine)rhenium(V). The same reaction sequence is consistent with the observed role of ethanol in the formation of bis(methyltriphenylphosphonium) hexachlororhenate in the reaction of stock chloroform, oxotrichlorobis(triphenylphosphine)rhenium(V) and excess triphenylphosphine. This sequence of reactions also provides a route which accounts for the extra chlorine needed to form

the tetrachlorobis(triphenylphosphine)rhenium(IV) and tetrachlorobis-(triphenylphosphine oxide)rhenium(IV) and the hexachlororhenate anion.

Three products were found when pure chloroform, oxotrichlorobis-(triphenylphosphine)rhenium(V) and excess triphenylphosphine reacted in a sealed tube. Reference to the sequence of reactions provides several postulated formulations which are consistent with the data obtained. The formulations which best describe the various compounds all involve some form of the moiety $\left[(C_6H_5)_3\overset{+}{P}CXY\overset{+}{P}(C_6H_5)_3\right]$ (where X=H or Cl, Y=H). A green material is formed, and when formulated as dichloromethylbis-(triphenylphosphonium) hexachlororhenate(IV), fits well with the data obtained. A formulation of methylenebis(triphenylphosphonium chloride) provides modest agreement with the observed data. A purple powder is also produced which, though several possible formulations were examined, remains an uncharacterized material.

Sealed tube reactions involving acetone and oxotrichlorobis(triphenylphosphine)rhenium(V) produced only intractable materials, not the expected dichlorotris(triphenylphosphine oxide)acetonerhenium(II), as reported (47). The reaction of 2-butanone with trichlorobis(triphenylphosphine)rhenium was found to produce trichloro(triphenylphosphine oxide)rhenium(III) as reported by Leitheiser (47).

These results show the unique role which the solvent has in the chemistry of rhenium(V) chloride. Solution studies of this material are dominated by the way in which the solvent interacts with rhenium(V) chloride either by reaction, as in the case of 1,4-dioxane, diethyl ether, acetone and acetic acid, or by only very limited interaction,

as in the case of carbon tetrachloride, chloroform and cyclohexane. The purity of the solvent and the solvent itself are important, as shown by sealed tube reactions in which the purity of the solvent altered the product(s) obtained.

APPENDIX

TABLE XXVIII

d-VALUES FOR OXOTETRACHLORORHENIUM(VI)

d-Value	Intensity
5.42	M
5.06	S
4.44	S
3.83	W
3.63	W
3.57	W
3.49	W
3.14	M
3.00	M
2.65	S
2.40	M
2.15	W
1.92	W

TABLE XXIX

d-VALUES FOR RHENIUM(III)CHLORIDE

d-Value	Intensity
8.11	VW
6.63	S
6.08	VW
5.08	VW
4.38	W
3.68	W
3.37	W
3.27	W
2.94	W
2.74	W
2.69	W
2.43	M
2.37	W
2.25	M
2.19	M
2.02	M
1.93	M
1.87	W
1.85	M
1.78	M
1.62	W
1.27	M
1.25	W

TABLE XXX

d-VALUES FOR RHENIUM(IV)CHLORIDE

d-Value	Intensity	d-Value	Intensity
6.23	VW	1.99	M
5.99	M	1.96	M
5.69	W	1.89	W
5.51	S	1.85	VW
4.47	M	1.83	VW
4.21	M	1.79	M
3.38	VW	1.77	VW
3.13	W	1.75	W
3.04	W	1.72	VW
2.92	W	1.70	VW
2.78	M	1.67	W
2.72	MS	1.62	VW
2.67	W	1.58	VW
2.61	W	1.55	VW
2.57	M	1.51	VW
2.37	VW	1.48	VW
2.26	W	1.46	VW
2.22	W	1.44	VW
2.16	W	1.41	VW
2.09	M	1.39	VW
2.06	M	1.38	VW
2.03	W	1.37	M

TABLE XXXI

d-VALUES FOR SOLUTE RECOVERED
FROM CARBON TETRACHLORIDE SOLUTION

d-Value	Intensity
5.37	S
4.37	W
2.73	VW

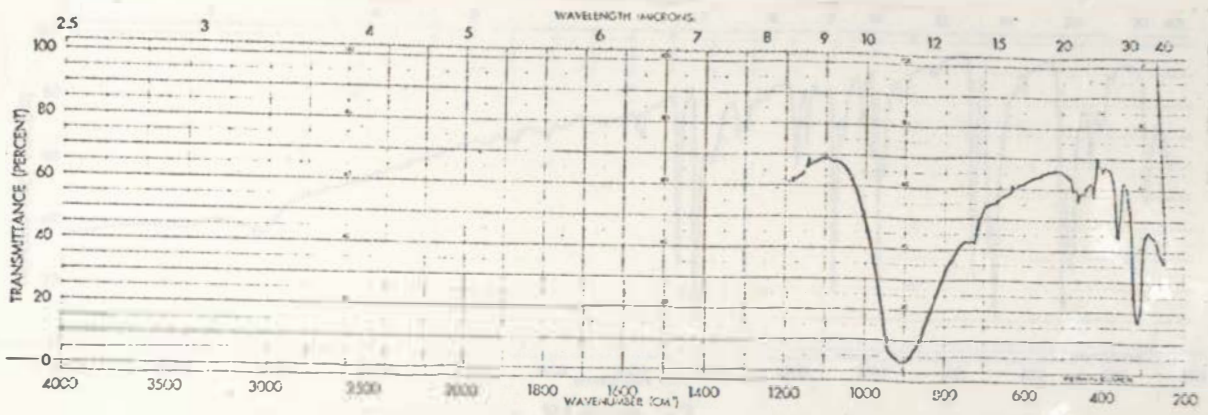


Figure 10

Ammonium Perrhenate

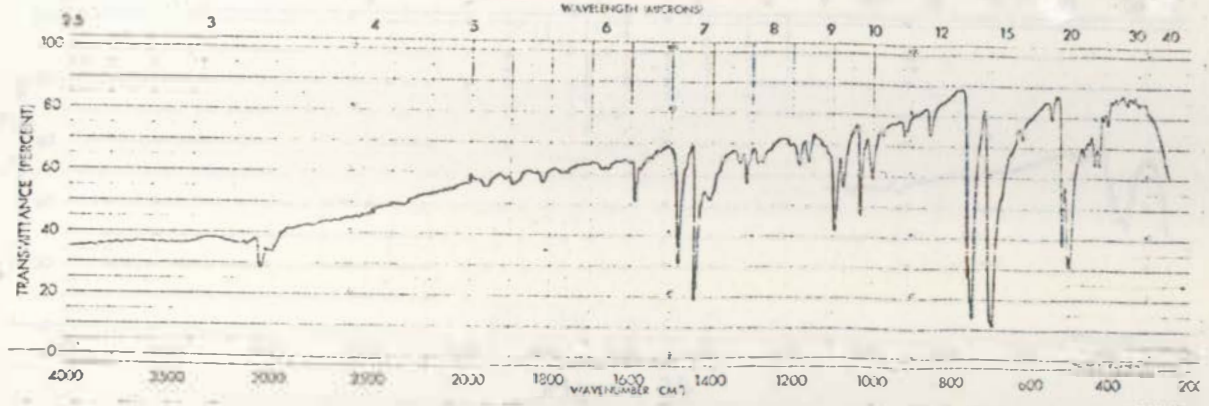


Figure 10

Triphenylphosphine

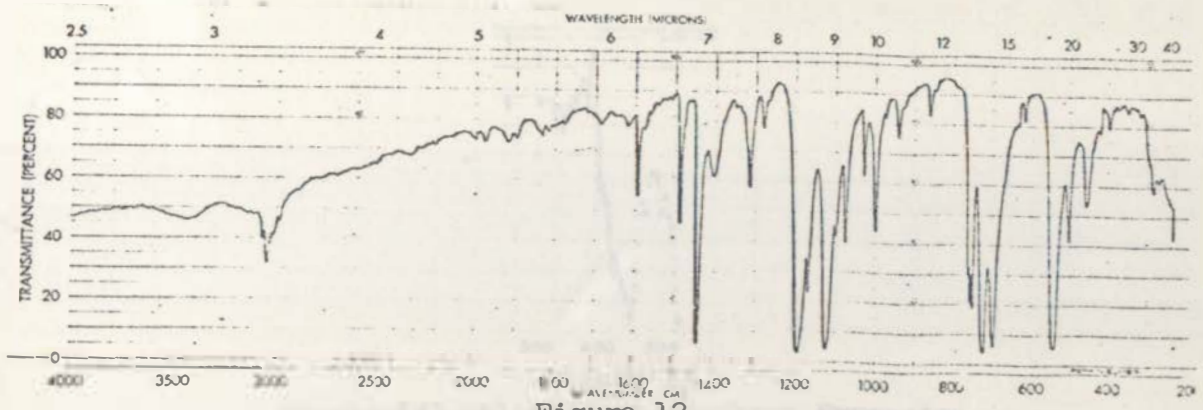


Figure 12

Triphenylphosphine Oxide

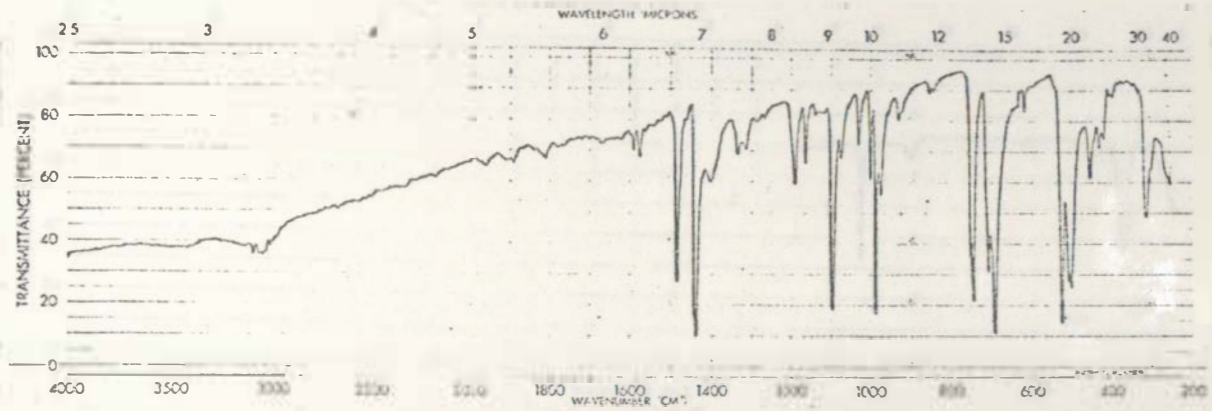


Figure 13

Oxotrichlorobis(triphenylphosphine)rhenium(V)

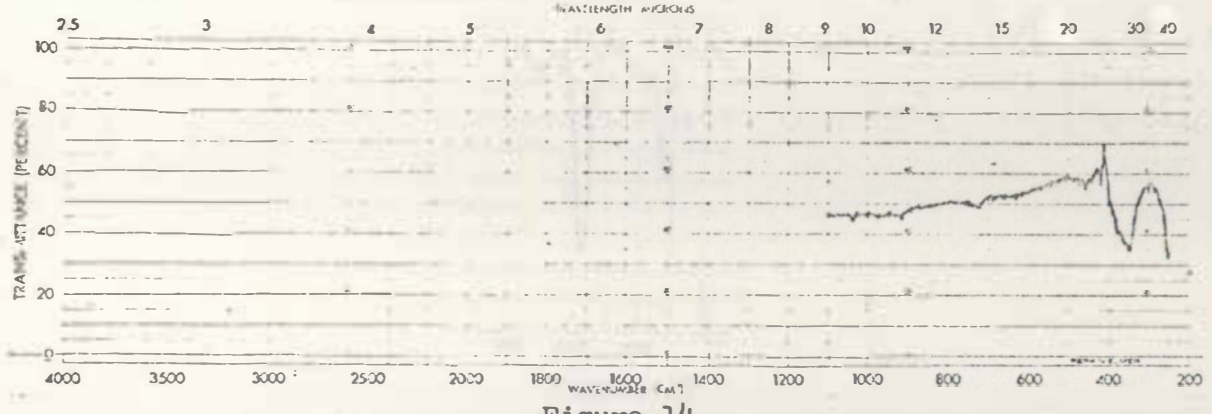


Figure 14

Rhenium(V) Chloride

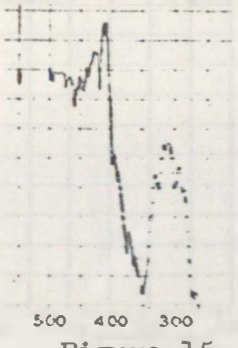


Figure 15

Rhenium(V) Chloride 2X Abscissa Expansion
of the 500 cm^{-1} to 250 cm^{-1} Region

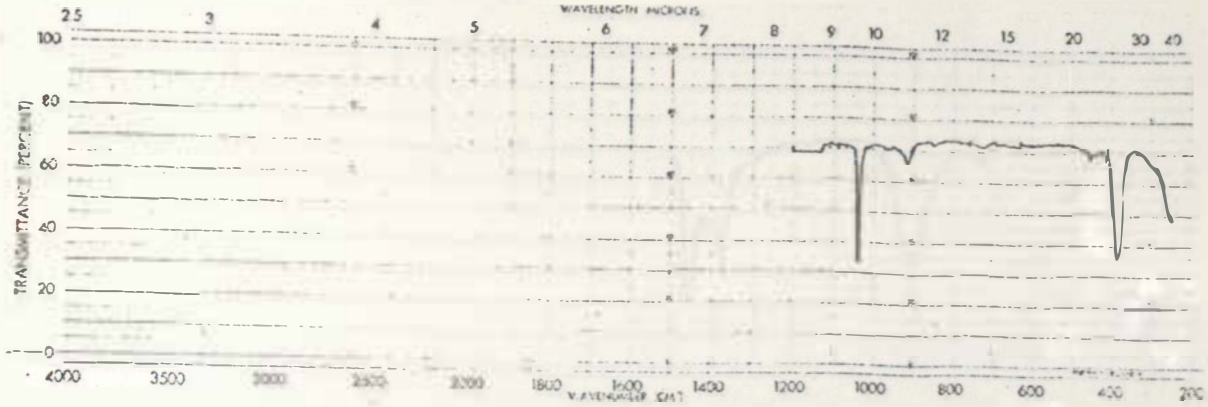


Figure 16

Oxotetrachlororhenium(VI)

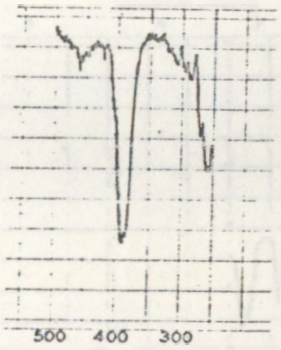


Figure 17

Oxotetrachlororhenium(VI) 2X Abscissa Expansion of the 500 cm^{-1} to 250 cm^{-1} Region

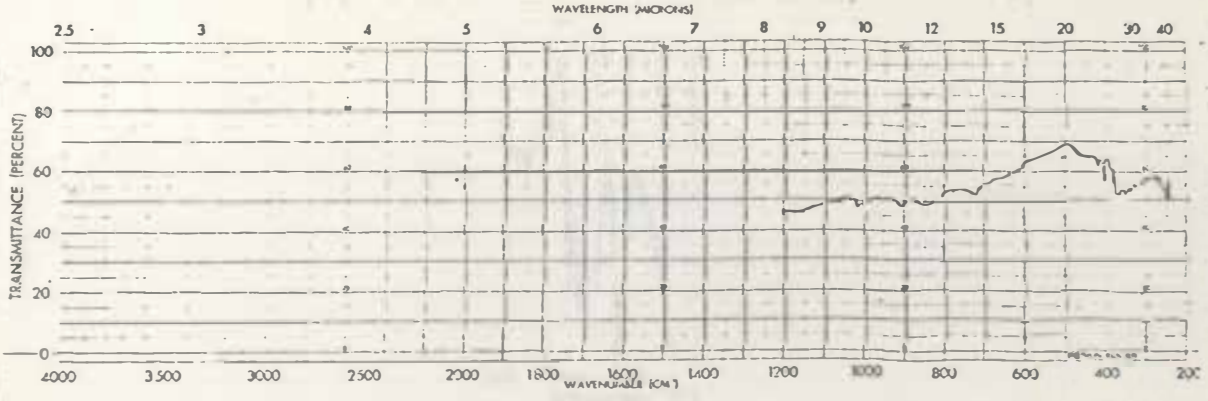


Figure 18

"Aged" Rhenium(V) Chloride

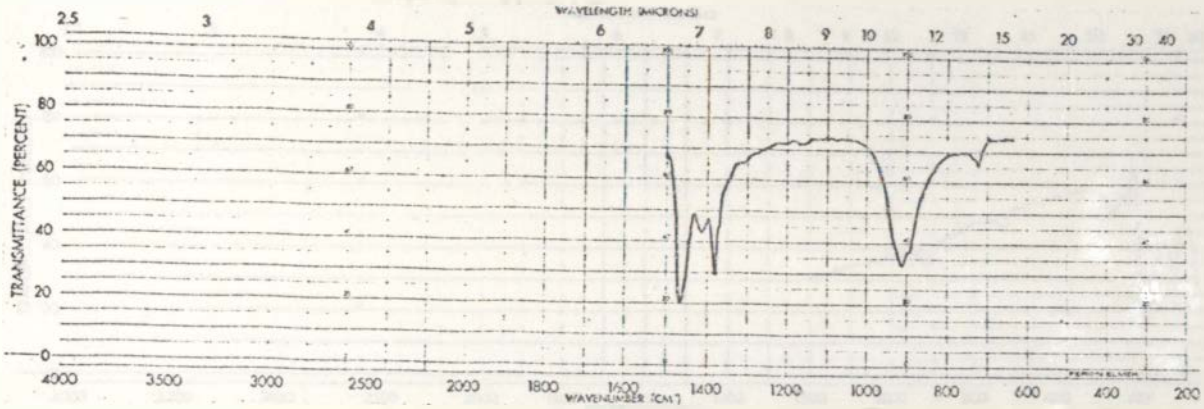


Figure 19

Rhenium Dioxide

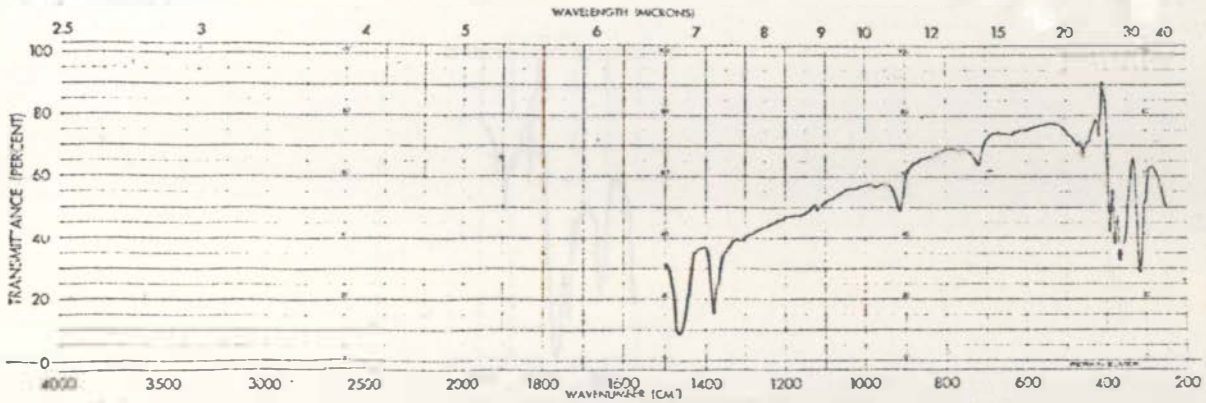


Figure 20

Rhenium(III) Chloride

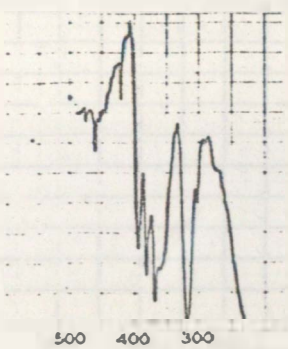


Figure 21

Rhenium(III) Chloride 2X Abscissa Expansion
of the 500 cm^{-1} to 250 cm^{-1} Region

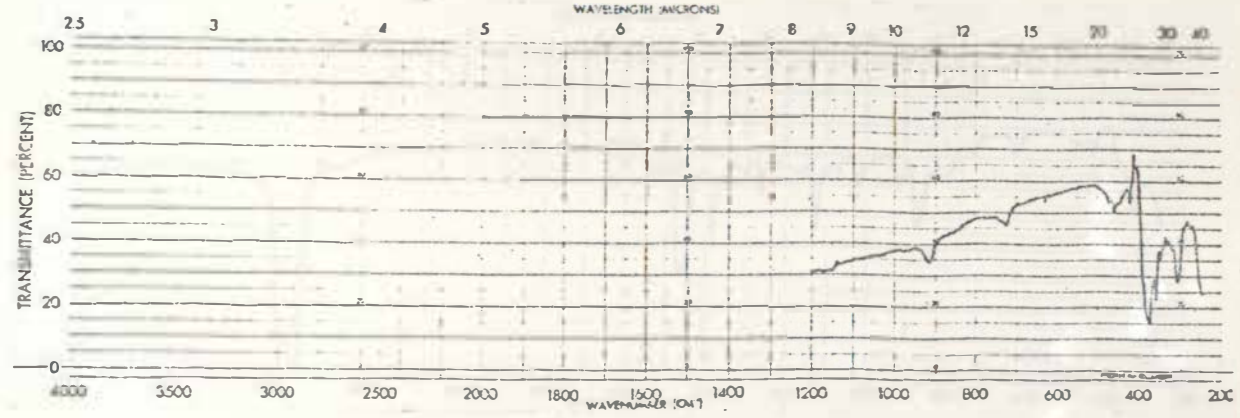


Figure 22

Rhenium(IV) Chloride

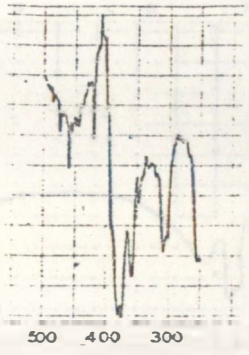


Figure 23

Rhenium(IV) Chloride 2X Abscissa Expansion
of the 500 cm^{-1} to 250 cm^{-1} Region

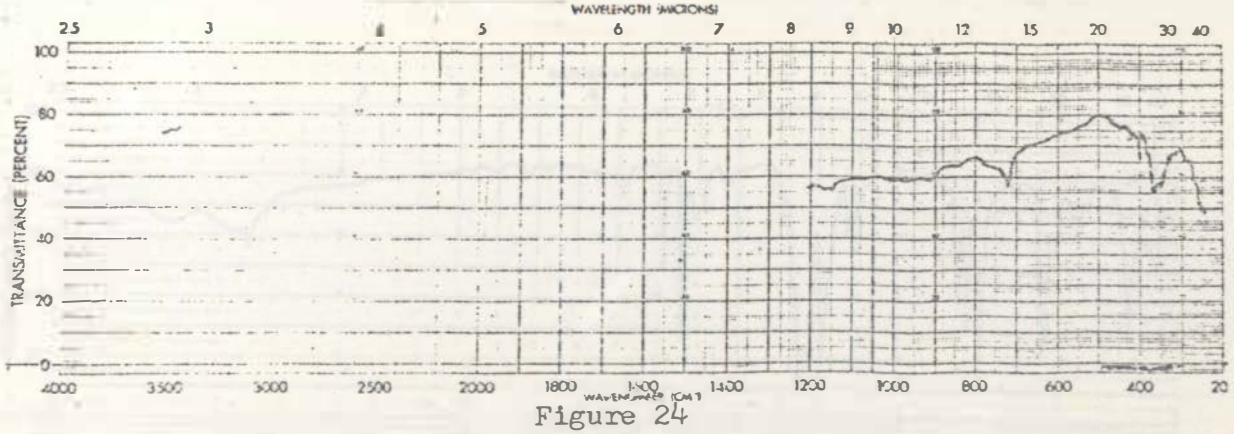


Figure 24

Recovered Material from Solution with Carbon Tetrachloride

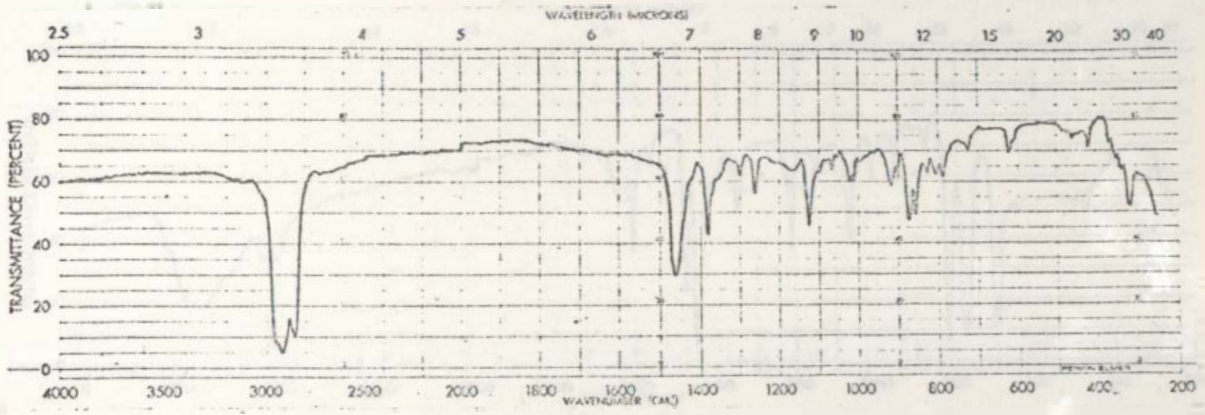


Figure 25

Tetrachlorobis(1,4-dioxane)rhenium(IV)

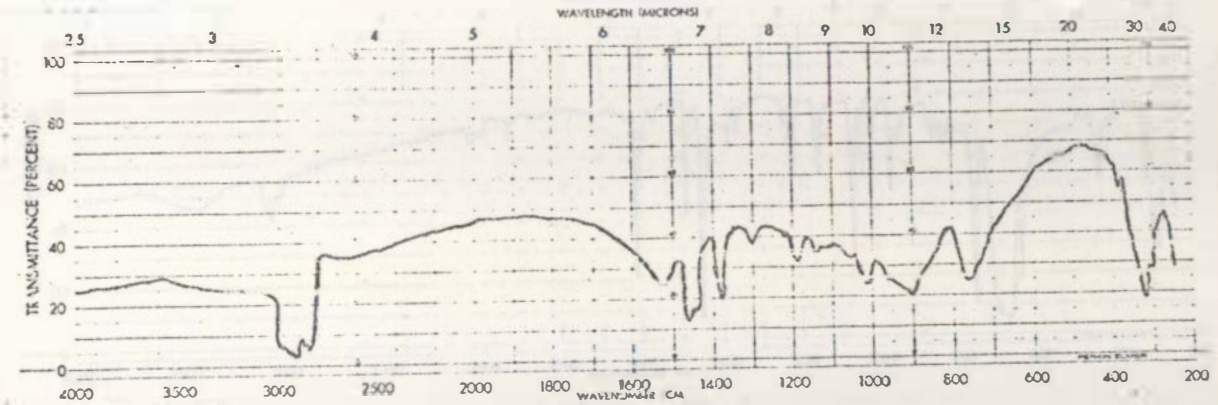


Figure 26

Recovered Material from Solution with Diethyl Ether

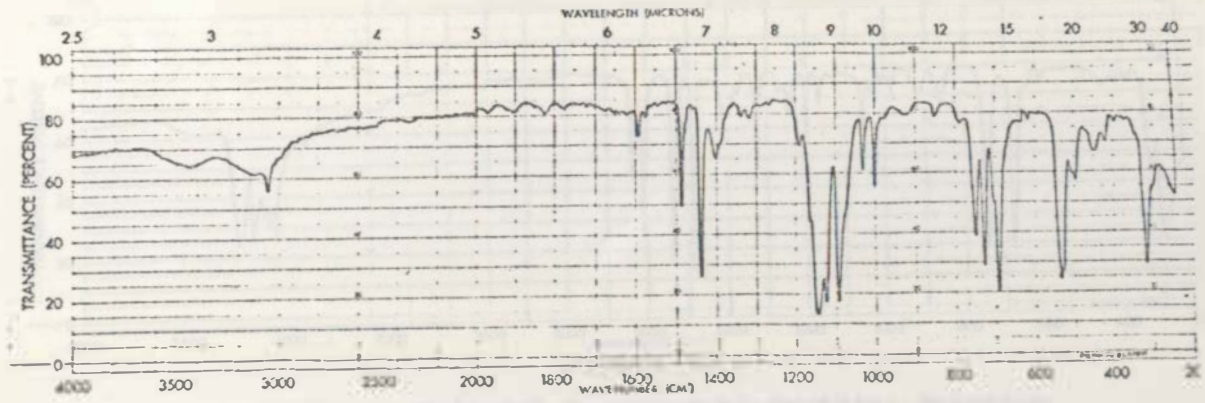


Figure 27

Tetrachloro(triphenylphosphinetriphenylphosphine oxide)rhenium(IV)

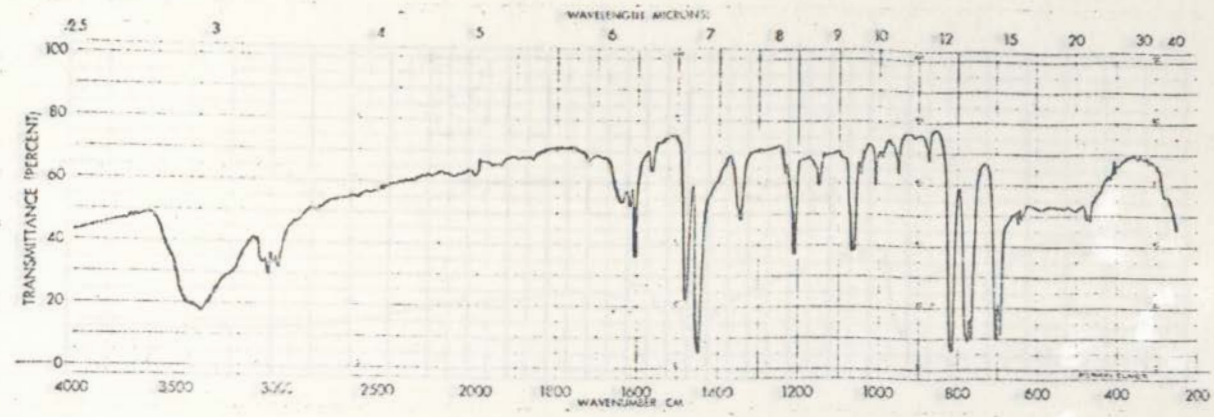


Figure 28

Dioxotetrakis(pyridine)rhenium(V) Chloride Dihydrate

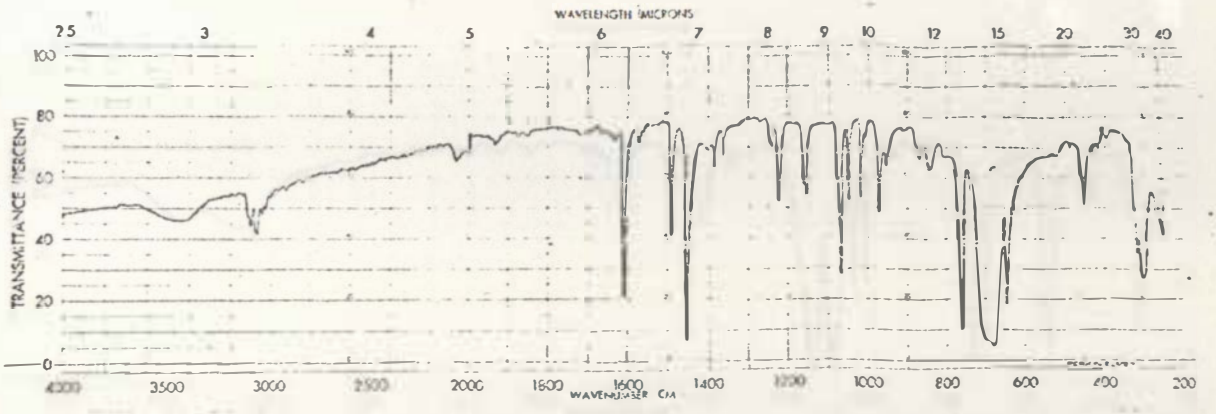


Figure 29

μ-oxodioxotetrachlorotetrakis(pyridine)dirhenium(V)

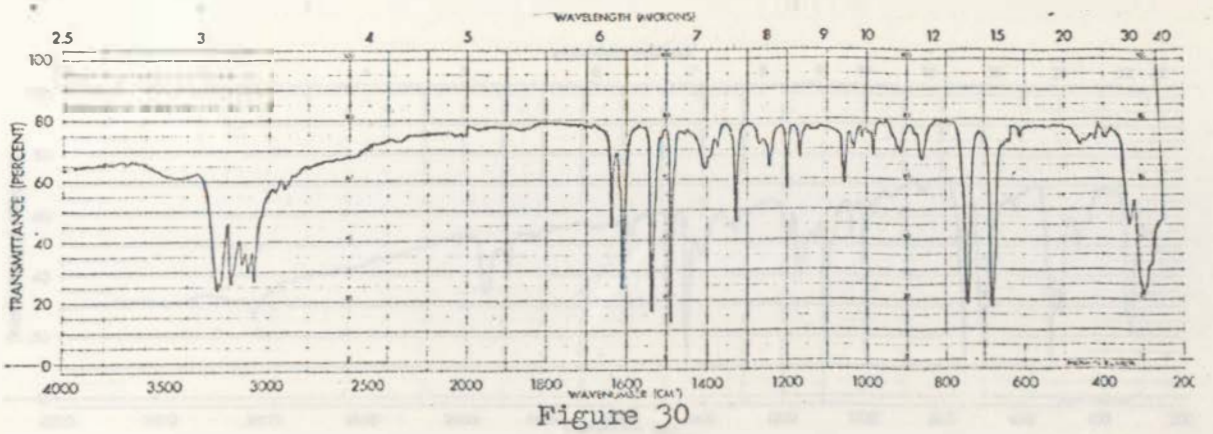


Figure 30

Gray-green Material Produced in Pyridine Reaction

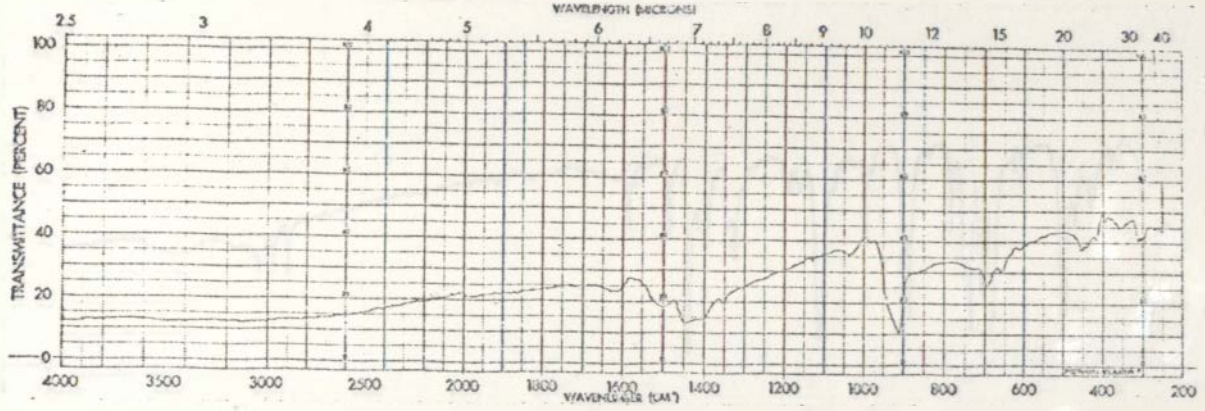


Figure 31

Material Produced in Acetic Acid Reaction

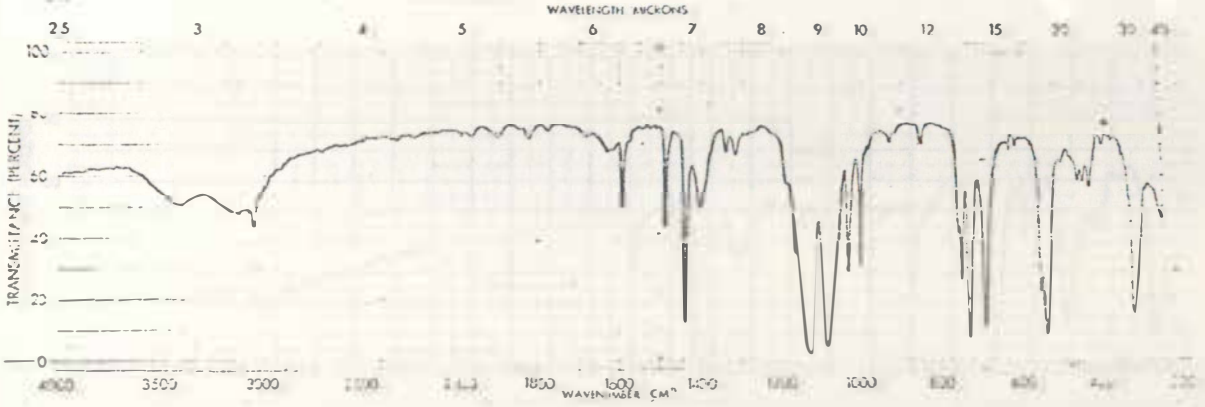


Figure 32

Tetrachlorobis(triphenylphosphine oxide)rhenium(IV)

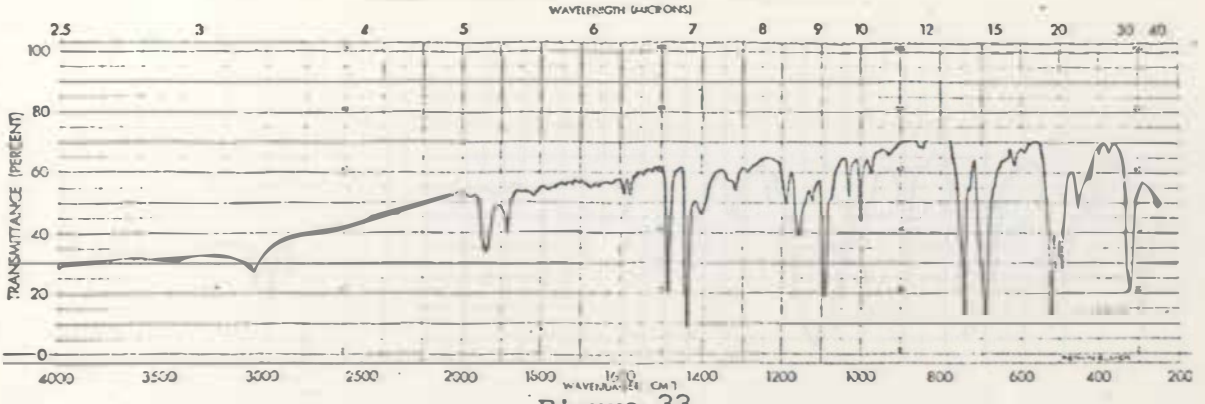


Figure 33

Tetrachlorobis(triphenylphosphine)rhenium(IV)

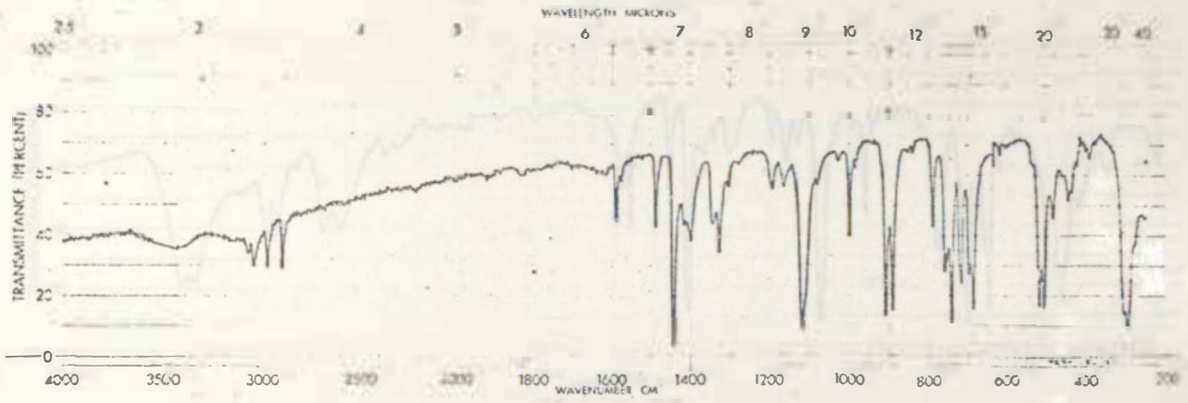


Figure 34

Bis(methyltriphenylphosphonium)hexachlororhenate(IV)

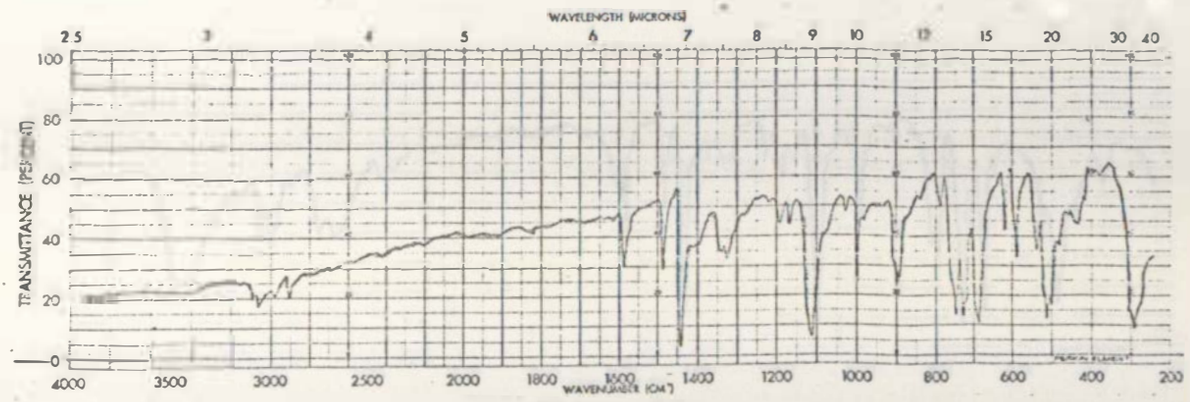


Figure 35

Material Produced in Reaction where Water Was
Added to Chloroform, Crude

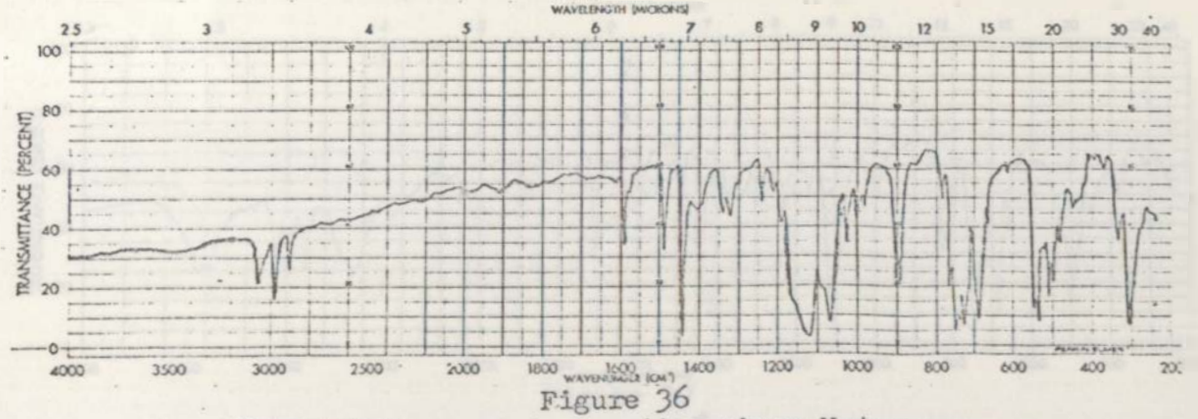


Figure 36

Material Produced in Reaction where Water was
Added to Chloroform, After Recrystallization Attempt

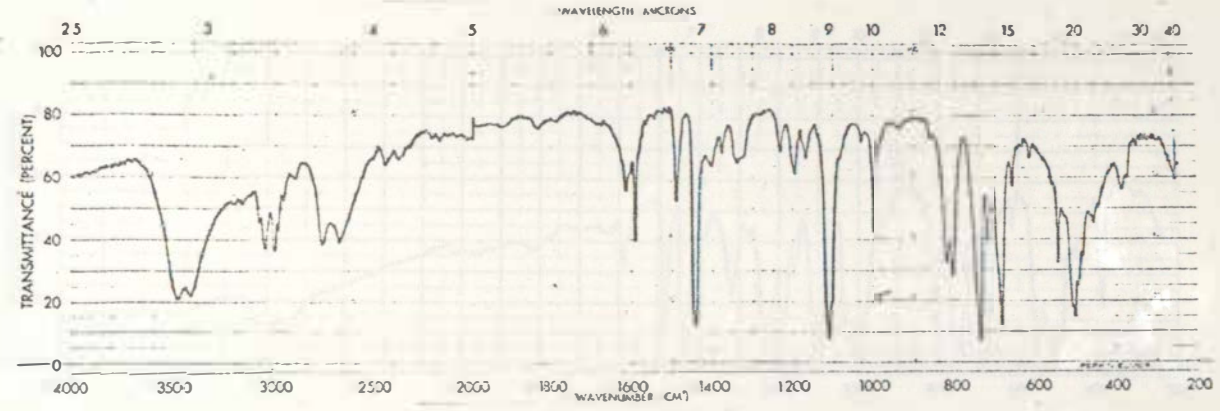


Figure 37

White Powder Produced in Chloroform Reaction, Crude

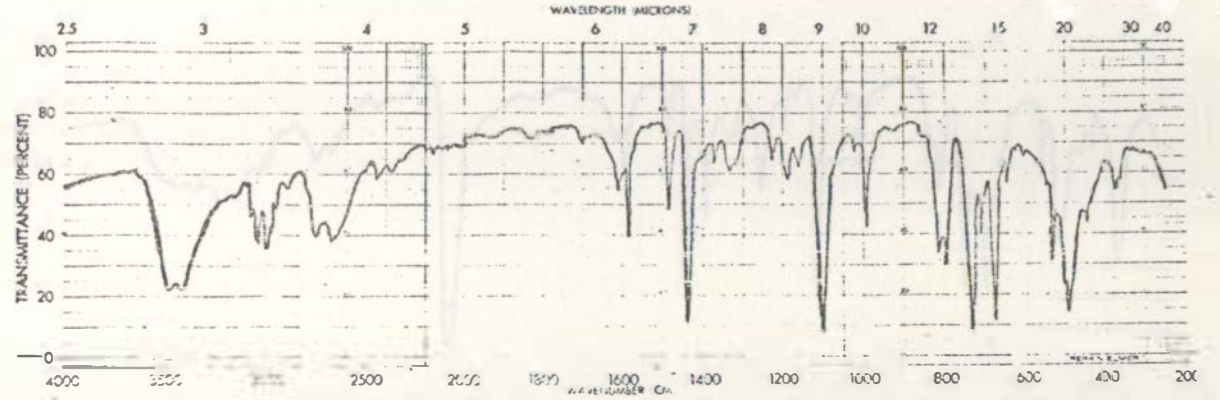


Figure 38

White Powder Recrystallized

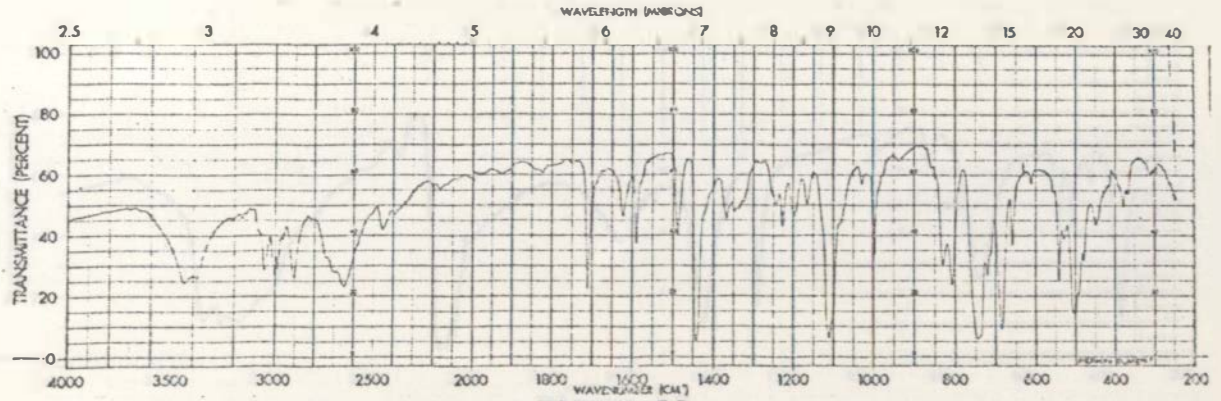


Figure 39

White Solid Heated to 80°C at 0.1 Torr

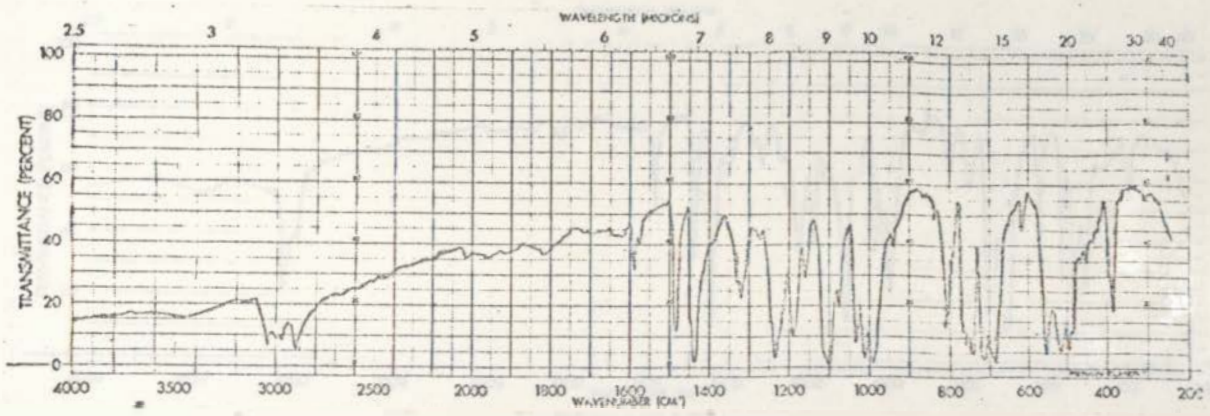


Figure 40

White Solid Heated to 140°C at 1 Atmosphere

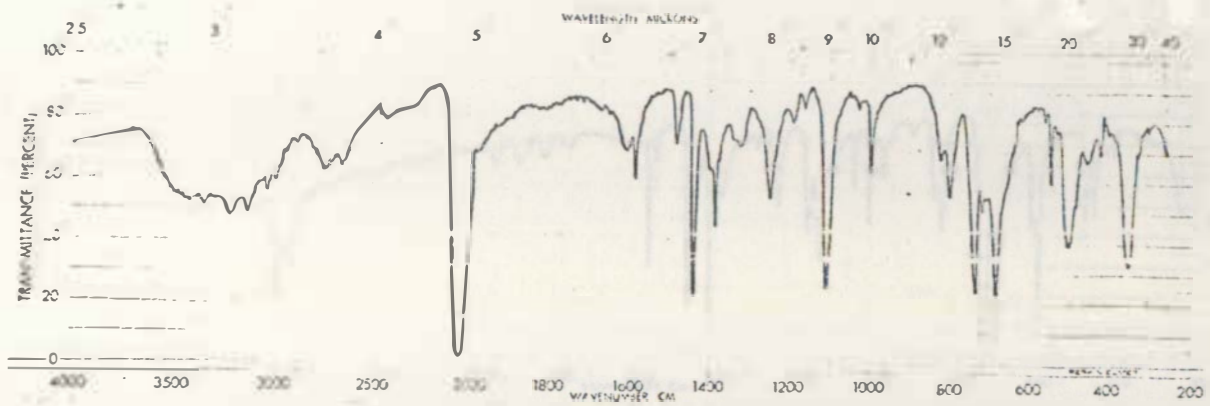


Figure 41

Tetrathiocyanatodiamminechromate(III) Salt
of White Powder

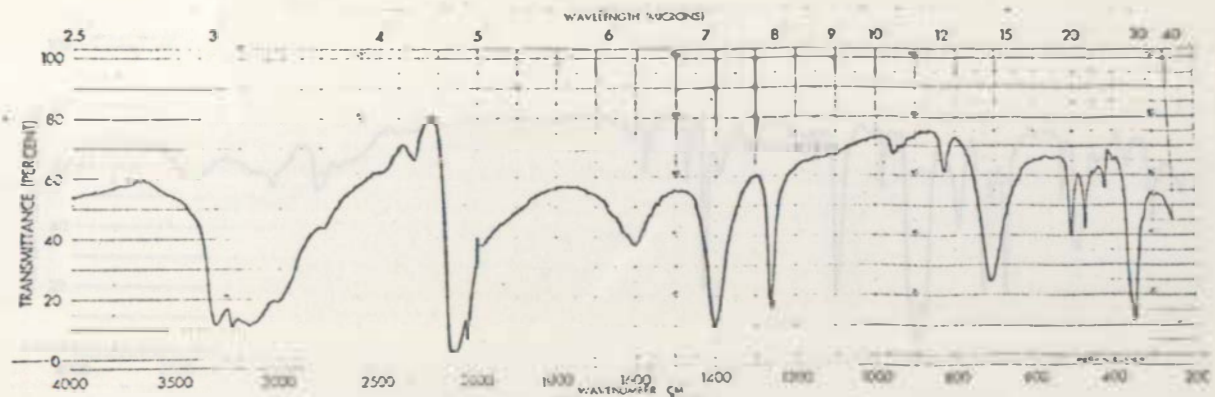


Figure 42

Ammonium Tetrathiocyanatodiamminechromate(III) Hydrate

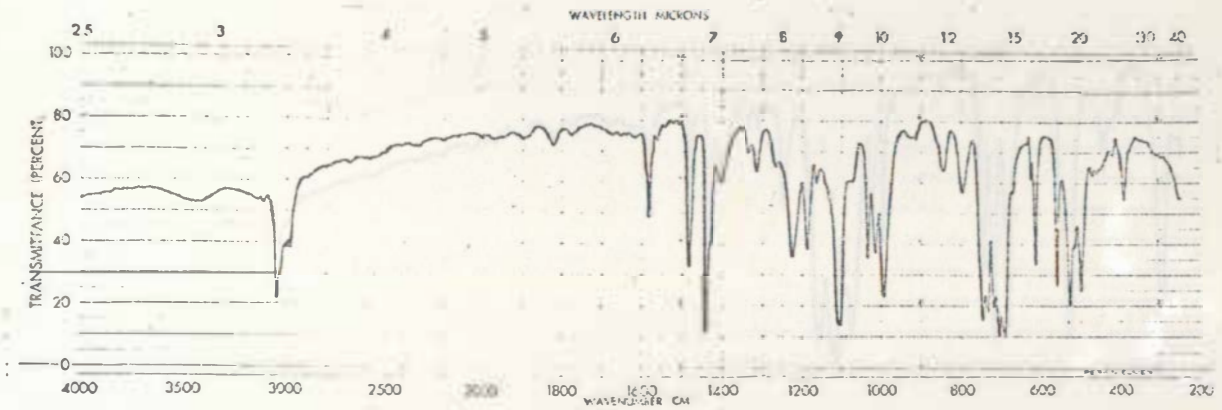


Figure 43

Tetraphenylborate Salt of White Powder

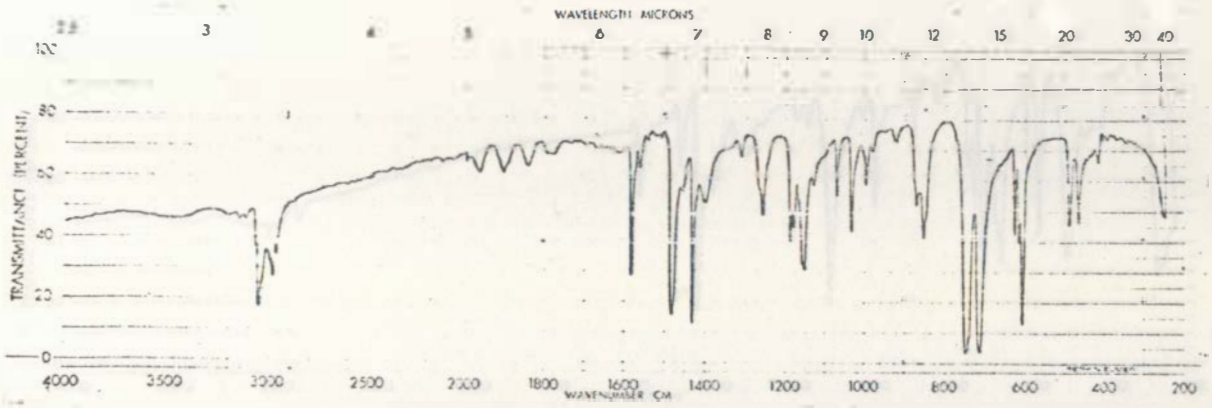


Figure 44

Sodium Tetraphenylborate

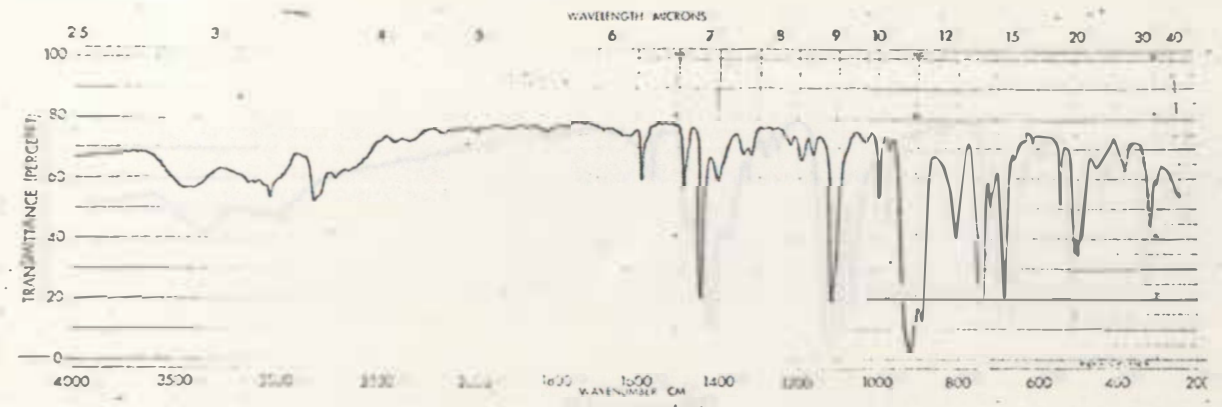


Figure 45

Perrhenate Salt of White Powder

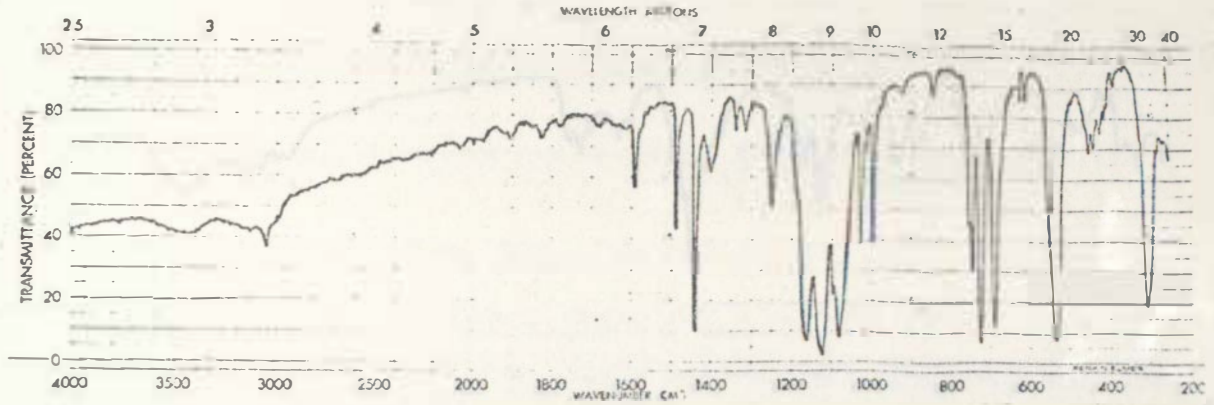


Figure 46

Purple Powder Produced in Chloroform Reaction

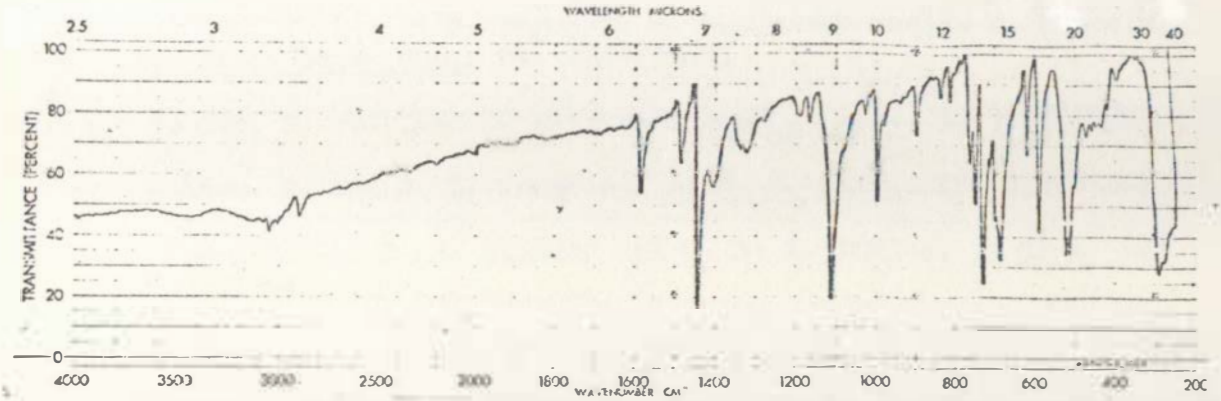


Figure 47

Dichloromethyltriphenylphosphine pentachloro-
(triphenylphosphine oxide)rhenium(IV)

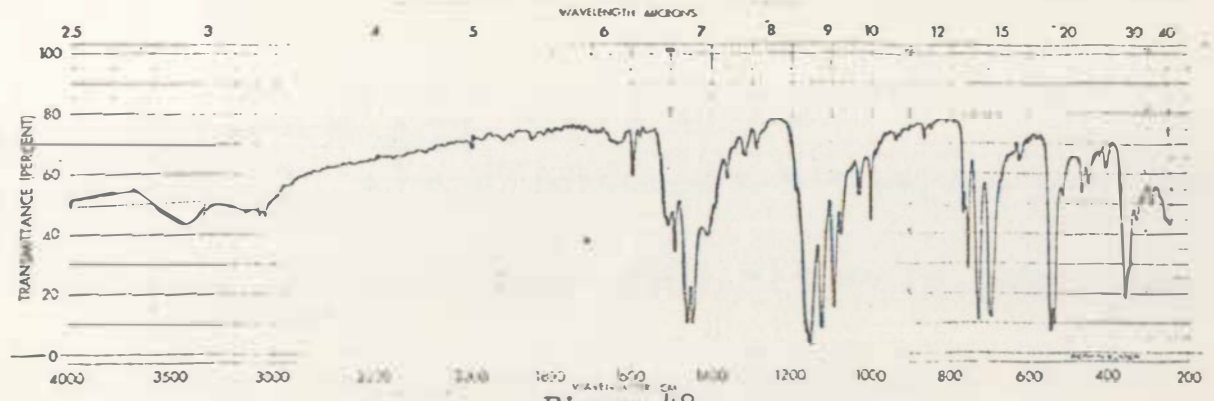


Figure 48

Trichloro(triphenylphosphine oxide)rhenium(III)

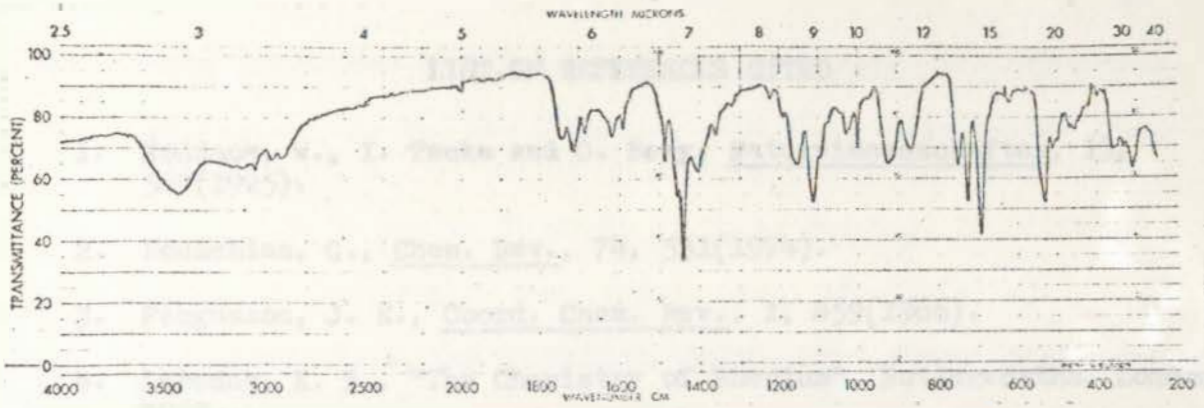


Figure 49

Green Solid Produced from 2-butanone Reaction

LIST OF REFERENCES CITED

1. Noddack, W., I. Tacke and O. Berg, Naturwissenschaften, 13, 567(1925).

2. Rouschias, G., Chem. Rev., 74, 531(1974).

3. Fergusson, J. E., Coord. Chem. Rev., 1, 459(1966).

4. Lebedev, K. B., "The Chemistry of Rhenium", Butterworths, London, 1962.

5. Colton, R., "The Chemistry of Rhenium and Technitium", Interscience Publishers, New York, 1965.

6. Cotton, F. A. and R. A. Walton, Inorg. Chem., 5, 1802(1966).

7. Cotton, F. A., M. J. Bennett, B. M. Foxman and P. F. Stokely, J. Amer. Chem. Soc., 89, 2759(1967).

8. Gehrke, H. Jr., and G. Eastland, Inorg, Chem., 9, 2722(1970).

9. Colton, R. and J. B. Tompkins, Aust. J. Chem., 19, 759(1966).

10. Allen, E. A., B. J. Brisdon and G. W. A. Fowles, J. Chem. Soc., 4531(1964).

11. Mucker, K., G. Smith and Q. Johnson, Acta Crystallogr., 874(1968).

12. Geilman, W., Fr. W. Wrigge and G. W. Blitz, Z. Anorg. Allg. Chem., 214, 244(1933).

13. Hurd, L. C. and E. Brimm, Inorg. Syn., 1, 180(1939).

14. Knox, K., S. Y. Tyree, Jr., R. D. Srivastave, V. Norman, J. Y. Bassett, Jr. and J. H. Holloway, J. Amer. Chem. Soc., 79, 3358 (1957).

15. Gluvkhov, I. A., S. B. Daridyants, M. A. Yunvsor and N. A. El'manova, Zh. Neorg. Khim., 6, 1264(1961).

16. Barduwil, A. B., F. N. Collier and S. Y. Tyree, Jr., Inorg. Chem., 3, 149(1964).

17. Horner, W. W., F. N. Collier and S. Y. Tyree, Jr., Inorg. Chem., 3, 1388(1964).

18. Zalkin, A. and D. E. Sands, Acta. Crystallogr., 11, 615(1958).

19. Sands, D. E. and A. Zalkin, Acta. Crystallogr., 12, 723(1959).

20. Smardzewski, R. R., Ph. D Thesis, Iowa State University, Ames, Iowa, 1969.

21. Edwards, D. A. and R. T. Ward, J. Chem. Soc.(A), 1617(1970).

22. Gehrke, H. Jr., and D. Bue, Inorg. Syn., 12, 193(1970).

23. Canterford, J. H. and R. Colton, Inorg. Nucl. Chem. Lett., 4, 607(1968).

24. Briscoe, H. V. A., P. L. Robinson and A. J. Rudge, J. Chem. Soc., 1104(1932).

25. Burgess, J., C. J. W. Fraser, I. Haigh and R. D. Peacock, J. Chem. Soc., Dalton Trans., 501(1973).

26. Horner, W. W., F. N. Collier and S. Y. Tyree, Jr., Inorg. Chem., 3, 1388(1964).

27. Johnson, N. P., F. I. M. Taha and G. Wilkinson, J. Chem. Soc., 2614(1964).

28. Johnson, N. P., C. J. L. Lock and G. Wilkinson, J. Chem. Soc., 1054(1964).

29. Cotton, F. A., W. R. Robinson and R. A. Walton, Inorg. Chem., 6, 223(1967).

30. Rouschias, G. and G. Wilkinson, J. Chem. Soc. (A), 489(1968).

31. Allen, E. A., N. P. Johnson, D. T. Rosevear and W. Wilkinson, J. Chem. Soc. (A), 788(1969).

32. Kepert, D. L. and R. Mandyczewski, J. Chem. Soc. (A), 530(1968).

33. Wardlow, W. and H. W. Webb, J. Chem. Soc., 2100(1930).

34. Alexander, K. M. and F. Fairbrother, J. Chem. Soc., S223(1949).

35. Fergusson, J. E., "Halogen Chemistry", Gutmann, Ed., Academic Press, Inc., London, 1967.

36. Anderson, S. and A. Astrom, Acta. Chem. Scand., 18, 2233(1964).

37. Knox, K., S. Y. Tyree, Jr., R. D. Srivastava, V. Norman, J. Y. Bassett and J. H. Holloway, J. Amer. Chem. Soc., 79, 3359(1957).

38. Bradley, D. C., B. N. Chakravorti and W. Wardlow, J. Chem. Soc., 2381(1956).

39. Schafer, H. and C. Pietruck, Z. Anorg. Allgem. Chem., 267, 174 (1951).

40. Glukhov., I. A., S. S. Eliseev and M. S. Pulatov, Russ. J. Inorg. Chem., 15, 730(1970).

41. Cotton, F. A. and G. Wilkinson, "Advanced Inorganic Chemistry", 3rd Ed., Interscience Publishers, New York, 1972.

42. McCarley, R. E., B. G. Hughes, J. C. Boatman and B. A. Torp, Adv. Chem. Ser., 37, 243(1963).

43. Larson, M. L., J. Amer. Chem. Soc., 82, 1223(1960).

44. Feenan, K. and G. W. A. Fowles, J. Chem. Soc., 2449(1965).

45. Cowley, A. H., F. Fairbrother and N. Scott, J. Chem. Soc., 3133 (1958).

46. Fairbrother, F., J. F. Nixon and H. Prophet, J. Less-Common Metals, 9, 434(1965).

47. Leitheiser, M., Masters Thesis, South Dakota State University, Brookings, South Dakota, 1969.

48. Willard, H. H. and G. M. Smith, Ind. Eng. Chem., 11, 305(1939).

49. Meloche, V. W., R. L. Martin and W. H. Webb, Anal. Chem., 29, 527(1957).

50. Niederl, J. B. and V. Niederl, "Micromethods of Quantitative Organic Analysis", John Wiley and Sons, Inc., New York, 1942.

51. Weissberger, A., E. S. Proskauer, J. A. Riddick and E. E. Toops, "Technique in Organic Chemistry", 2nd ed, Vol. VII, Interscience Publishers, Inc., New York, 1955.

52. Vogel, A. I., "A Text-book of Practical Organic Chemistry", Longmans Green and Co., New York, 1948.

53. Eastland, G., Doctoral Thesis, South Dakota State University, Brookings, South Dakota, 1969.

54. Gehrke, H. Jr., Doctoral Thesis, University of Iowa, Iowa City, Iowa, 1964.

55. Schlenk, W. and A. Thal, Ber., 46, 2840(1913).

56. Herzog, S., J. Dehuert and K. Lubdes, "Technique of Inorganic Chemistry," p 119, Vol 7, Interscience Publishers, New York, 1968.

57. Shriver, D. F., "The Manipulation of Air-sensitive Compounds," p 145, McGraw Hill Book Company, New York, 1969.

58. Guest, A. and C. J. L. Lock, Can. J. Chem., 49, 603(1971).

59. Adams, D. M., "Metal-Ligand and Related Vibrations", St. Martin's Press, New York, 1968.

60. Matheson Gas Products, Catalog No. 30, Lyndhurst, New Jersey.

61. Azaroff, L. V. and M. J. Buerger, "The Powder Method", McGraw Hill Book Company, New York, 1958.

62. Grove, D. E. and G. Wilkinson, J. Chem. Soc. A., 1224(1966).

63. Frais, P. W., C. J. L. Lock and A. Guest, Chem. Comm., 75(1971).

64. Calvo, C., P. W. Frais and C. J. L. Lock, Can. J. Chem., 50, 3607(1972).

65. Willard, H. H., L. L. Merritt and J. A. Dean, "Instrumental Methods of Analysis", 5th Edition, D. Van Nostrand Co., New York, 1974.

66. Walton, J. R., Masters Thesis, Purdue University, Lafayette, Indiana (1957).

67. Taha, F. and G. Wilkinson, J. Chem. Soc., 5406(1963).

68. Al-Mowali, A. H. and A. L. Porte, J. Chem. Soc., Dalton, 50(1975).

69. Bellamy, L. J., "The Infra-red Spectra of Complex Molecules", John Wiley and Sons, Inc., New York, 1958.

70. Cotton, F. A., S. J. Lippard and J. T. Mague, Inorg. Chem., 4, 508(1965).

71. Colton, R., R. Levitus and G. Wilkinson, J. Chem. Soc., 4121(1960).

72. Hass, L., Masters Thesis, South Dakota State University, Brookings, South Dakota, 1970.

73. Deacon, G. B. and J. H. S. Green, Spectrochim. Acta., 24A, 845(1968).

74. Deacon, C. B. and J. H. S. Green, Spectrochim. Acta., 25A, 355 (1969).

75. Chatt, J., J. D. Garforth, N. P. Johnson and G. A. Rowe, J. Chem. Soc., 601(1964).

76. Edwards, A. J., J. Chem. Soc. Dalton, 582(1972).

77. Brisdon, B. J. and D. A. Edwards, Inorg. Chem., 7, 1898(1968).

78. Silverstein, R. M. and G. C. Bassler, "Spectrophotometric Identification of Organic Compounds", John Wiley and Sons, New York, 1967.

79. Gehrke, H. Jr., unpublished observation.

80. "Standard Infrared Spectra", Sadtler Research Laboratories, Spectrum number 15-B, Philadelphia, 1959.

81. Gill, N. S., R. H. Nuttall, D. E. Scaife and D. W. A. Sharp, J. Inorg. Nucl. Chem., 18, 79(1961).

82. Losinski, R., unpublished observations.

83. Holm, P. L., unpublished observations.

84. Chatt, J. and G. A. Rowe, Chem. and Ind., 92(1962).

85. Lock, C. J. L., and G. Wilkinson, Chem. and Ind., 40(1967).

86. Rouschias, G. and G. Wilkinson, J. Chem. Soc. (A), 465(1966).

87. Corbridge, D. E. C., Topics in Phosphorus Chemistry, 6, 235(1969).

88. Hooz, J. and S. S. H. Gilani, Can. J. Chem., 46, 86(1968).

89. Burn, A. J. and J. S. G. Cadogen, J. Chem. Soc., 5788(1963).

90. Zhmurova, I. A., A. Kisilenko and A. Kirsanov, J. Gen. Chem. U. S. S. R., 32, 2544(1962).

91. Rabinowitz, R. and R. Marcus, J. Amer. Chem. Soc., 84, 1312(1962).

92. Ramierez, F. and N. McKelvie, J. Amer. Chem. Soc., 79, 5829(1957).

93. Ramierez, F., N. B. Desai and N. McKelvie, J. Amer. Chem. Soc., 84, 1745(1962).

94. Hudson, R. F., "Structure and Mechanism in Organo-Phosphorus Chemistry", p 151ff, Academic Press, New York, 1965.

95. Grim, S. O., L. C. Satek, C. A. Tolman and J. P. Jenson, Inorg. Chem., 14, 656(1975).

96. Grisley, D. W., Tetrahedron Letters, 435(1963).

97. Grisley, D. W., J. C. Alm and C. N. Matthews, Tetrahedron, 21, 5(1965).

98. Speziale, A. J. and K. W. Ratts, J. Amer. Chem. Soc., 84, 854 (1962).

99. "Handbook of Chemistry and Physics", 51st Ed., R. E. Weast, Ed., p F-179, The Chemical Rubber Co. Cleveland, Ohio, 1970.

100. Arzoumanidis, G. G., Chem. Comm., 217(1969).

101. Gehrke, H. Jr., Private Communication.

102. Worman, J. J., Private Communication.

103. Driscoll, J. S. and C. N. Matthews, U. S. Pat. 3, 374, 256 (March 19, 1968).

104. Ramierez, F., N. B. Desai, N. Hansen and N. McKelvie, J. Amer. Chem. Soc., 83, 3539(1961).

105. Driscoll, J. S., D. W. Grisley, J. V. Prustinger, J. E. Harris and C. N. Matthews, J. Org. Chem., 29, 2427(1964).

106. Issleib, K. and R. Lindner, Justus Liebigs Ann. Chem., 707, 120(1967).

107. Mark, V., C. Dungan, M. Crutchfield and J. Van Wazer, Topics in Phosphorus Chemistry, 5, 227(1967).

108. Bonati, F. and F. A. Cotton, Inorg. Chem., 6, 1353(1967).